KINETIC AND STRUCTURAL STUDIES IN ARENEDIAZONIUM SALT CHEMISTRY

by

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A thesis submitted for the degree of Doctor of Philosophy at the University of Warwick (Department of Chemistry and Molecular Sciences).

July 1980

Before coming here I was confused about this subject. Having listened to your lecture I am still confused but on a higher level.

Enrico Fermi

Declaration

The content of this thesis is, to the best of my knowledge, original although certain sections of the introduction are loosely based on similar parts of my M.Sc. thesis.

The crystal mounting and collection of data for the structure determination were performed by Dr N.W. Alcock who also assisted me with the computation of the results.

ACKNOWLEDGEMENTS

I would like to thank Professor T.J. Kemp for his guidance and constant encouragement given throughout the course of this work. My thanks go also to my colleagues, especially Dr. N.W. Alcock for his help with the determination of the crystal structures, Dr. H.B. Ambroz for plotting the e.s.r. spectrum, Dr. G.A. Quick for the use of the rate constant determination computer programme and Dr. A. Cox and Mr P. Pinot de Moira for many helpful discussions. I would also like to thank Mr A.H. Wiles, Mr E. Burgess and Mrs P. Compton for their assistance in the design and construction of the quenched stopped-flow apparatus. Finally, I am indebted to Ozalid Ltd., (Loughton, Essex), whose financial support through a C.A.S.E. Studentship made this work possible.

ABSTRACT

The kinetics and mechanisms of the reactions of arenediazonium cations, ArN_2^+, with a selection of suitably activated naphthalene-based coupling compounds, including some of particular industrial significance, have been investigated over a wider pH range than before. The dependence of the coupling rate constant on both ring substituents on the arenediazonium cations and the steric and electronic effects of substituent groups on the coupler have been rationalised. It has been shown that the σ^+-constants give a better correlation than the Hammett σ-constants for the rate coefficients for the reaction of ArN_2^+ with the commercially important sodium 2,3-dihydroxynaphthalene-6-sulphonate. When used as a buffer, borax drastically modifies the rate constant -pH profile of certain coupling reactions as a result of the production of a cyclic complex between the coupler and borate ions.

The crystal structure of an aryldiazotate, namely disodium syn-benzenediazotate-4-sulphonate, has been determined for the first time, and the diazotate group shown to exhibit a 'cis' configuration in contrast to the conclusion reached on kinetic grounds by Sterba.

The kinetics and mechanisms of the highly complex equilibria between ArN_2^+ and the corresponding aryldiazotates have been studied and some rate and equilibrium constants measured; these results, together with those from the literature, have been plotted against substituent constants to obtain ρ-values. Compounds having 2-substituents were included after determination of their σ-constants, although the data points from the 2,6-dichloro-4-nitro compound was found to deviate substantially from certain linear free energy relationships.

The large rate constant of the N-O bond splitting of syn-aryldiazohydroxides containing strongly electron-withdrawing substituents were measured with a purpose-built 'quenched stopped flow' apparatus. These values enabled extension of those already available to give a good Hammett plot.

CONTENTS

Abbreviations

A Absorbance

$^1A_1$, $^1B_1$ Singly degenerate energy level

a, b, c, α, β, γ Unit cell dimensions

[C], [ArO^-] Coupler concentration

[D], [ArN_2^+] Arenediazonium cation concentration

D Density

ε Extinction coefficient

F(100) Number of protons per molecule

ΔH_{ms} Line width (e.s.r.)

I Transmittance

k Rate constants (subscripts defined in text)

K Equilibrium constants (subscripts defined in text)

λ Wavelength

1-Naphthol 1-Hydroxynaphthalene

2-Naphthol 2-Hydroxynaphthalene

OD Optical density

R Resorcinol

ρ Reaction constant

σ Substituent constant

$t_{\frac{1}{2}}$ Half life

U Unit cell volume

μ Ionic strength

χ Substituent groups

Z Number of molecules per unit cell

The notations '2-, 3-, 4- etc.' are used in this thesis except in section 1.5 where 'ortho, meta and para' are utilised where they are more descriptive.

Abbreviations (continued).

P.P. Pariser and Parr

H.M.O. Huckel Molecular Orbital theory

During this study, all rate and equilibrium constants were measured at 25°C

The notations syn. and anti . represent n. and iso. and are not necessarily synonymous with cis. and trans.

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List of Publications

N.W. Alcock, T.J. Kemp and P.D. Goodman, Tet . Letters, 33, 3115 (1979).

N.W. Alcock, P.D. Goodman and T.J. Kemp, J.C.S. Perkin II, in the press, paper 9/1480.

A. Cox, P.D. Goodman, T.J. Kemp and P. Pinot de Moira, submitted for publication in the International Journal of Chemical Kinetics.

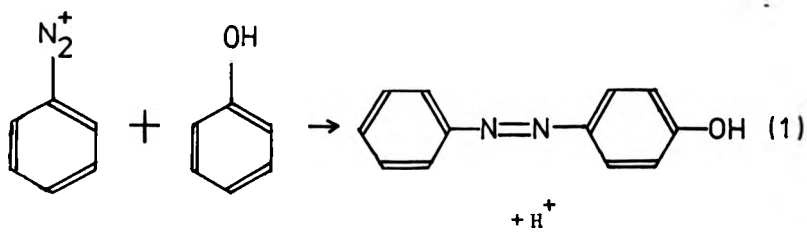
1. INTRODUCTION

1.1 Preface

The aim of this project has been to study the kinetics and mechanisms of the reactions of aromatic diazonium salts (or arenediazonium salts as we shall refer to them) with

(a) certain suitably activated aromatic compounds and

(b) hydroxyl ions at high pH. (a), the coupling reaction, e.g.



(1)

has been extensively studied ever since arenediazonium salts were first synthesised by Griess[1] in 1858. The reaction kinetics were first investigated by Goldschmidt[2] in 1897 and subsequently by many others (Section 1.3).

The coupling reaction has been used commercially on a wide scale for many years in the manufacture of azo dyes and pigments, e.g. 35,000 tons of azo dyes were produced in 1975 in the U.S.A. alone. It is also extensively utilised in the so-called dye-line reprographic process, of which details are given in Section 1.7. In the present study, the kinetics and mechanism of the coupling reaction between arenediazonium salts and a number of commercially important couplers have been studied both by conventional methods and with the aid of stopped-flow techniques.

(b) The coupling reaction at pH > 9.0 may often be complicated by reaction of the arenediazonium ion with hydroxyl ions to give aromatic diazotates (also known as aryldiazotates) and we have

therefore made a separate investigation of this reaction, mostly utilising stopped-flow methods. While this reaction has been known almost since the discovery of arenediazonium salts, it is only comparatively recently that a reasonable understanding of the equilibria involved has been achieved. Aryldiazotates are used in the azo dye industry as a stable, easily handled source of the corresponding relatively unstable arenediazonium salt. Despite their wide availability, there has been some controversy over details of their structure which has been finally resolved in this thesis (section 3.1).

1.2 Chemistry of arenediazonium salts

1.2.1 Preparation of arenediazonium salts

The most common methods for the preparation of arenediazonium salts involve the reaction of an aromatic amine with a source of incipient NO^+, and a list is given below. There are a number of sources of NO^+, e.g. from nitrous acid:[3]

$$HNO_2 + H^+ \longrightarrow H_2O - \overset{+}{N}O \longrightarrow NO^+ + H_2O$$

$$2HNO_2 \xrightarrow{-H_2O} N_2O_3 \longrightarrow NO^+ + NO_2^-$$

The diazotisation reaction is believed to proceed in four steps:[4]

$$Ar-NH_2 + NO^+ \xrightarrow{slow} Ar-\overset{H}{\underset{H}{\overset{|}{\underset{|}{\overset{+}{N}}}}}-NO \quad (2)$$

$$\downarrow -H^+$$

$$Ar-N-N=O$$

$$\downarrow fast$$

$$Ar-\overset{+}{N}\equiv N \xleftarrow[fast]{+H^+ \; -H_2O} Ar-N=N-OH$$

Methods

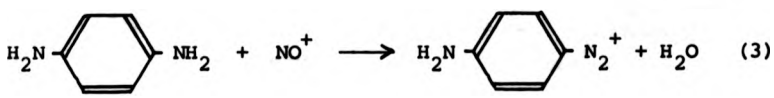
(i) Direct method.[5,6] This, the most commonly used method, involves the reaction of nitrous acid from an acidified solution of an alkali metal (usually sodium)nitrite with a suspension of the aromatic amine (as $ArNH_3^+$) in an excess of acid. This method can be used with most aromatic amines which are at least slightly soluble in aqueous acid and not too weakly basic.

(ii) Insoluble or more weakly basic amines can be diazotised by the inverted method whereby the amine is mixed with ice and sodium nitrite before the addition of acid.[5]

(iii) For even more weakly basic amines, such as 2,4-dinitroaniline, concentrated acid solvents are employed.[5] Usually concentrated sulphuric acid is mixed with sodium nitrite to obtain nitrosylsulphuric acid (HSO_4NO) which is then added to the amine. Witt[5] used nitric acid as the solvent which gives nitrous acid on the addition of sodium metabisulphite.

(iv) The preparation of solid, water-soluble arenediazonium salts may be carried out in non-aqueous solvents,[5,6] usually alcohols, with alkyl nitrites (often amyl nitrite) as the nitrosating agent.

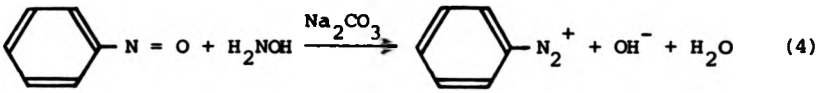
Bis-amino compounds can be either singly or doubly diazotised.[4] The direct method usually gives mono-diazonium salts, e.g.



(3)

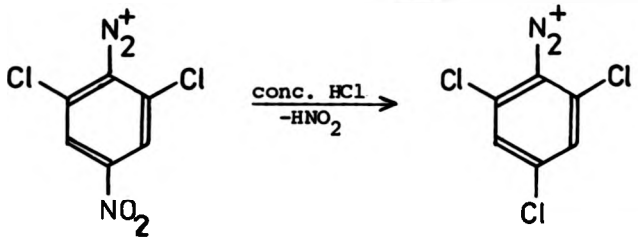
To obtain bis-diazonium compounds, more powerful nitrosating agents are required, e.g. 4-phenylenebisdiazonium salts can be synthesised from 4-phenylene diamine with either nitrosylsulphuric acid[5] or dinitrogen trioxide.[7]

Arenediazonium salts can be synthesised from other compounds apart from aromatic amines.[4,6] Various nitrosating agents are employed to obtain arenediazonium salts from aromatic imines or nitroso compounds.[4,6] Nitrosobenzene reacts with hydroxylamine thus:[6]



(4)

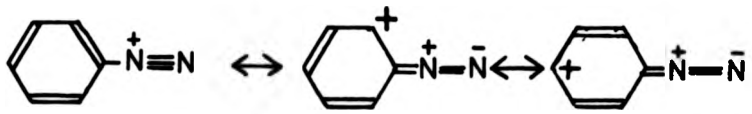
Finally, substitution reactions may be used to convert one arenediazonium salt into another, e.g.[4,8]



(5)

1.2.2 Stability of arenediazonium salts

Although arenediazonium salts are relatively unstable compounds, they are much more stable both kinetically and thermodynamically than alkyldiazonium salts. This is due to delocalisation of the positive charge from the diazonium group into the π-system of the ring,[9] viz.



(6)

(I) (II) (III)

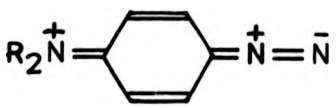
As solids, certain arenediazonium salts are prone to spontaneous, and even explosive, decomposition. Arenediazonium perchlorates have even been known to explode when wet.[10] The explosive nature of a few arenediazonium salts, such as diazotised

picramic acid, is exploited in their use as detonators.[11] For commercial use, solid arenediazonium salts are stabilised by preparing them as tetrafluoroborate, tetrachlorozincate or other similar complex salts.[6,12,13]

The stability of solid arenediazonium salts, while mainly governed by the nature of the anion, is also influenced by the presence of substituent groups on the benzene ring. This becomes the major factor controlling their stability in solution. In general, electron-withdrawing groups (e.g. 4-nitro) decrease stability and electron-donating groups (e.g. 4-alkylamino) increase it, although there are exceptions (e.g. 4-methoxy). This is discussed in Section 1.2.5.

1.2.3 Structure of arenediazonium salts

The basic structure of arenediazonium salts is well defined. While the unsubstituted cation has the structure (I), the extent of delocalisation due to participation of structures (II) and (III) is unclear due to conflicting evidence. It has been suggested by Zollinger[9] that electron-donating 4-substituents (e.g. 4-dialkylamino-) enhance the resonance contributions via (IV).



(IV)

This view has been supported as follows.

(i) P.P. calculations by Sukigara and Kikuchi[14] show that as the electron-donating capability of the substituent group increases, the N-N bond order decreases. This indicates that

there is an increasing contribution from the quinoidal form (II).

(ii) The ultraviolet spectra of diazophenols[15,16] and 4-amino-benzenediazonium salts[17,18] suggest a large contribution from the quinoidal structure (II).

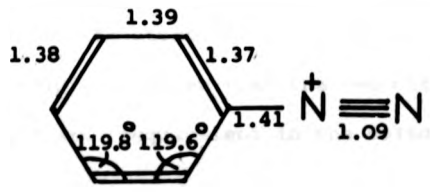
(iii) The N ≡ N and Ar - N vibrational stretching frequencies are dependent on ring substituents;[19] the ρ values for the Hammett plot of σ against ν(N ≡ N) and ν(Ar - N) for arene-diazonium salts with electron-donating substituents is less than that obtained from arenediazonium salts with electron-withdrawing substituents (i.e. the complete plot shows a distinct break). This is thought[20] to be due to contributions from structures like (IV).

The infra-red spectra[21] of diazophenols exhibit an N ≡ N stretching vibration at relatively low frequency, ca. 2000 cm^{-1}, and a carbonyl vibration at ca. 1600. This indicates a large contribution from (VI).

(V) (VI)

However, conflicting evidence comes from X-ray crystallographic data. The first X-ray study to be performed on an arenediazonium salt was by Romming in 1963.[22] The structure of benzenediazonium chloride was found to be (VII).

Interatomic distances (Å)



(VII)

The angles and interatomic distances indicate that the contributions from the resonance structures (II) and (III) are very small. The ring is somewhat distorted, which is not surprising as the diazonium group is the most powerful electron-withdrawing group known (σ = 1.81).[7] The C - N bond distance is intermediate between those typical of C - N and C = N, and the N - N bond distance corresponds to that expected for N ≡ N.

Although bond distances are not very sensitive to bond order, these observations indicate that the positive charge is principally on the nitrogen atom adjacent to the ring.[22] However, Porai-Koshits has suggested[23] that as the chloride counter-ion lies almost equidistant from the nitrogen atoms, the positive charge is shared between them. Certain other substituted arenediazonium salts have also been characterised by X-ray analysis. These include 2-methoxy-,[24] 4-N,N-dimethylamino-[25] and 4-morpholino-benzenediazonium salts,[26] all of which were predicted[9] to have s substantial contribution from their quinoidal forms (II) and (III). The Ar - N and N ≡ N bond distances in the 4-N,N-dimethylamino- compound are substantially longer than those in the unsubstituted arenediazonium salt; however, there is some doubt as to the accuracy of these results. The X-ray crystal structures of the 2-methoxy[24] and 4-morpholino[26] salts have inter-atomic bond distances in their diazonium groups which are the same as in the unsubstituted compound.[22] This indicates that there are no contributions from structures (II) and (III). The benzene rings are somewhat distorted with slightly larger bond distances; however, HMO calculations on the latter compound have failed to rationalise its structure.[27] ^{15}N-Isotopic substitution of the diazonium group has shown that the two nitrogen atoms do not exchange, and are inequivalent in the solid state.[28]

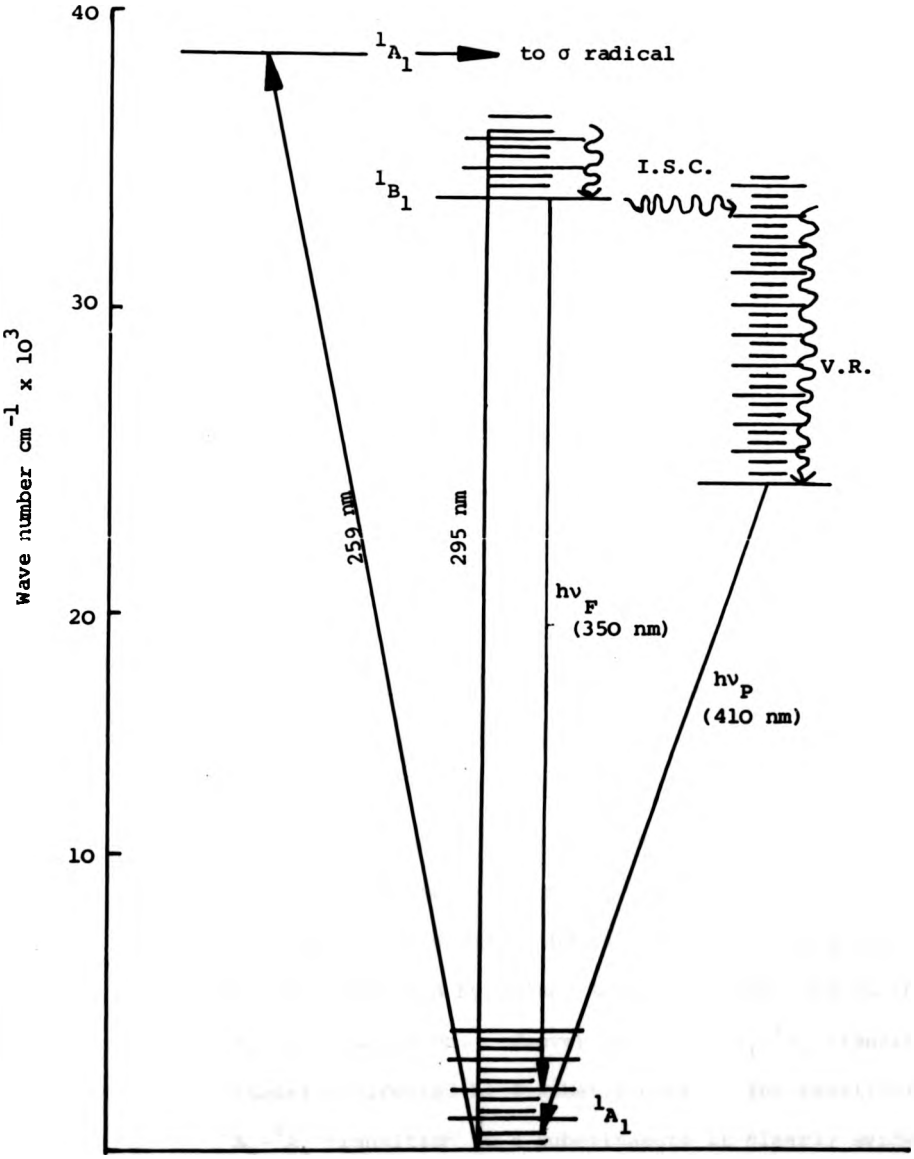


Figure 1 Jablonski diagram for benzenediazonium tetrafluoroborate

I.S.C. = inter-system crossing

V.R. = vibrational relaxation

Subscripts F and P denote fluorescence and phosphorescence respectively

In conclusion, it seems likely that the resonance contributions (II) and (III) play some role in the stability of the arenediazonium salt, especially with alkoxyl and dialkylamino substituents at the 2- and 4-positions, but to what extent seems unclear.

1.2.4 The ultraviolet spectra of arenediazonium salts

Arenediazonium salts can be regarded as substituted benzene compounds, exhibiting the typical benzene absorption bands, i.e. from 200 nm to 450 nm, most arenediazonium salts show two $\pi \rightarrow \pi^*$ transitions.[29] Typical is benzenediazonium tetrafluoroborate, which in ethanol has absorption bands, at 259 nm and 295 nm.[14] Sukigara and Kikuchi,[14] on the basis of calculations similar to the method of Pariser and Parr, attributed them to $^1A_1$-$^1A_1$ and $^1A_1$-$^1B_1$ transitions respectively. On irradiation with 295 nm light, fluorescence and phosphorescence are observed, but with 259 nm light, an e.s.r. signal due to a phenyl σ-radical was detected (Fig. 1).[30]

Evleth and Cox[29] computed the electron densities for the ground and excited $^1A_1$ and $^1B_1$ states. These indicate that in the ring there is a lower electron density in the excited state compared to the ground state, and consequently electron-donating substituents should have a greater stabilizing effect on the excited states than the ground state. From their calculations, they also proposed that the $^1A_1$-$^1B_1$ transitions should be more strongly affected by 2- and 3-methoxy substituents than the $^1A_1$-$^1A_1$ transition. Conversely, the $^1A_1$-$^1A_1$ transitions are primarily affected by 4-substituents. The sensitivity of the $^1A_1$-$^1A_1$ transition to 4-substituents is clearly evident (Table 1).[30]

Table 1

λ_{max} of the u.v. spectra of substituted arenediazonium cations

4-substituent	λ_{max} (nm)
-H	259
$-NO_2$	360
$-OCH_3$	313
$-(CH_3)_2N$	380

whereas the sensitivity of the $^1A_1$-$^1B_1$ transition to 3-substituents is demonstrated by a comparison of the spectra of 3-substituted arenediazonium salts (Table 2)[14].

Table 2

λ_{max} of $^1A_1$-$^1A_1$ and $^1A_1$-$^1B_1$ transitions of substituted arenediazonium salts

Substituent	λ $^1A_1$-$^1A_1$ (nm)	λ $^1A_1$-$^1B_1$ (nm)
H	259	295
F	262	308
Cl	266	317
Br	268.5	323
OCH_3	273.5	348

Only one absorption band is observed with some 4-substituted arenediazonium salts, [14] e.g. 4-methoxy and 4-chloro. This is because the strong $^1A_1$-$^1A_1$ transition has been more strongly red shifted than the weaker $^1A_1$-$^1B_1$ transition, and so effectively masks it.

1.2.5 Thermal decomposition of arenediazonium salts

Zollinger has recently reviewed the thermal dediazoniation of arenediazonium ions [31]. Decomposition is known to proceed by two fundamentally different pathways with a number of variants depending on the solvent and the presence of additives such as oxygen, pyridine etc. The two fundamental pathways are

(i) homolytic, which involves a radical intermediate:-

$$ArN_2^+X^- \longrightarrow Ar^\cdot + N_2 + X^\cdot \qquad (7)$$

and (ii) the heterolytic mechanism which involves an aryl cation:-[32]

$$ArN_2^+ \longrightarrow Ar^+ + N_2 \qquad (8)$$

In the solid state, arenediazonium salts undergo decomposition *via* the Schiemann reaction (9)[33]:-

$$Ar - N_2^+BF_4^- \longrightarrow ArF + N_2 + BF_3 \qquad (9)$$

In acidic solution, decomposition is usually first-order[34] but is second-order for 4-phenylene-bis-diazonium salts.[11] Reasonable general correlation between the thermal decomposition rate constants and the σ-constants of the ring substituents of 22 arenediazonium salts has been found by Schulte-Frohlinde, both kinetically[35] and by a theoretical approach,[36] but with certain exceptions. The 4-methoxy compound is exceptionally stable, possibly due to resonance with a quinoidal structure (see Section 1.2.3). Swain *et al.*[32,37] obtained an excellent correlation using a four-parameter equation, and this includes the 4-methoxy compound. The rate of thermal decomposition below pH 7 is independent both of pH and the acid medium. The reaction is (10), where X^- is either from the counter-ion or the added acid:-

$$2ArN_2^+ \xrightarrow[H_2O]{X^-} ArOH + ArX + 2N_2 \qquad (10)$$

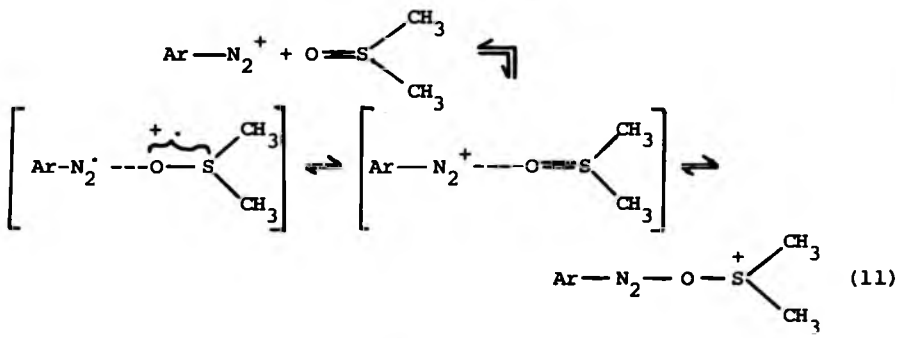
The ratio $[ArOH]/[ArX]$ is dependent on the initial concentration of the arenediazonium salt and the concentration of acid.[38] In basic solution, first the diazohydroxide and then the diazotate are produced (Section 1.4).

In non-aqueous media, a great many variations occur,[31] of which a few examples are listed here:-

(i) Alcohols. The mechanism for dediazoniation in methanol is a radical chain reaction involving the aryldiazo radical ($A - N = N^{\cdot}$).[39] There are a number of products, including ArH, $ArOCH_3$ etc. Ring substituents on the arenediazonium salt

influence both the rate and mechanism. Arenediazonium salts with weakly electrophilic substituents react predominantly via a heterolytic mechanism. Dissolved oxygen, being a radical scavenger, encourages the heterolytic pathway. The choice of alcohol solvent also affects the proportions of products, i.e. higher molecular weight alcohols tend to give more reduction products, i.e. ArH.[31]

(ii) Dimethylsulphoxide.Arenediazonium salts give charge-transfer complexes with this solvent, viz.[40]



(11)

The reaction then proceeds via a radical mechanism to give a variety of products depending on the ring substituents and any additives. The products include biphenyls, ArOH, Ar-$SOCH_3$ etc.[40]

(iii) Trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP). Lewis et al.[41] noticed,from isotope studies in aqueous solution with labelled nitrogen, a very small amount of $N_\alpha \rightarrow N_\beta$ rearrangement during hydrolysis.

$$Ar-N\equiv N^{15} \rightleftharpoons Ar-N^{15}\equiv N \qquad (12)$$

Reaction (12) in acidic solution was noticeable to only a small amount, but if genuine would be evidence for a free aryl cation. Zollinger[42] used TFE and HFIP, two weakly nucleophilic solvents, with a much greater solubility of nitrogen. These solvents do give a much greater proportion of $N_\alpha \rightarrow N_\beta$ rearrangement, and Zollinger concluded that the heterolytic mechanism (13) takes place:[42]

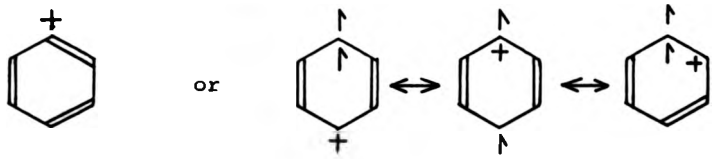
$$Ar - N_2^+ \rightleftharpoons |Ar^+N_2| \rightleftharpoons Ar^+ + N_2$$

$$\downarrow Nu^- \qquad\qquad \downarrow Nu^- \qquad (13)$$

$$Ar - Nu + N_2 \qquad Ar - Nu + N_2$$

$|Ar^+N_2|$ is regarded as a contact ion-molecule pair, but it is Ar^+ that exchanges with 'external' dissolved nitrogen.

The structure of the aryl cation is usually a singlet,[31] but arenediazonium salts with electron-donor substituents in the 4-position exist as a triplet state, featuring typical e.s.r. resonance,[43] i.e.



singlet (VIII) or triplet (IX)

The variety of mechanisms with different solvents can be explained by solvation of the arenediazonium salt. The thermal decompositon of arenediazonium cations shifts in favour of a homolytic pathway along the series of solvents as indicated:[31]

$\longrightarrow$ increasing tendency to homolysis

TFE, HFIP, acidic H_2O, acidic MeOH, DMSO

This trend follows four groups of constants: (i) the Gutmann donor and (ii) the Gutmann acceptor numbers, which give a measure of the donating and accepting capability of the solvents respectively, (iii) the Koppel and Pal'm constants and (iv) the Schleyer nucleophilic indices, which describe the nucleophilic properties of the solvent.[31] The correlation between the solvents and these constants demonstrates that solvation plays an important role in the reactions of ArN_2^+; however, the

complex nature of these reactions has still to be explained. Bunnett[44] has suggested that these two pathways proceed via a common intermediate, the 'activated diazonium ion' $(ArN_2^+)^*$.

$$ArN_2^+ \longrightarrow [ArN_2^+]^* \begin{cases} \nearrow \text{heterolytic to } Ar^+ \\ \searrow \text{homolytic to } Ar^\cdot \end{cases}$$

1.2.6 Reactions of arenediazonium salts

The reactions of arenediazonium salts have been extensively reviewed[5,6,9,45,46] and so only a brief summary is included here.

(i) The thermal decomposition of arenediazonium salts is discussed in Section 1.2.5. The photochemically induced decomposition involves additional reactions to thermolysis and is not completely understood. It depends on the environment and the chemical species present. The field has been reviewed by Calvert et al.,[47] Ruchardt et al.[48] and Ando.[49]

(ii) The diazonium group can be replaced by a wide variety of species.[49] These include:

(a) hydrogen, as in the thermal decomposition of arenediazonium salts in ethanol;

(b) halogen, as in the Sandmeyer and Gattermann reactions;[50]

(c) nitrogen from compounds such as ammonia which gives an azide;[51]

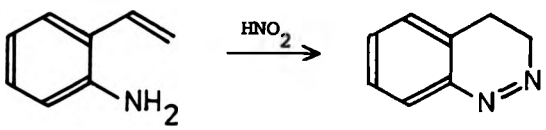
(d) oxygen to give phenols, alcohols and ethers;[46]

(e) carbon to make new carbon-carbon bonds, as in the Pschorr syntheses,[52] the Gomberg-Bachmann[53] and Meerwein reactions;[54]

(f) most other non-metallic elements such as with the sulphur of thiourea;[46]

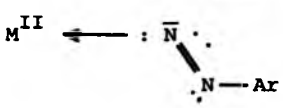
(g) arenediazonium salts form double salts with metals which, on decomposition, yield carbon-metal bonds.[46]

(iii) Reactions involving the diazonium group. These include the coupling reaction which is dealt with in Section 1.3, reactions with base (OH^-) to give diazotates (Section 1.4), and with many other nucleophiles such as -CN and $-SO_3^-$.[55] Zollinger[45] found that some species such as hydroxide and cyanide ions give products with a cis-azo group, whereas others such as phenols and tertiary amines give trans compounds. A useful synthetic pathway via arenediazonium salts to cinnolines is known,[46] e.g. the overall reaction (14)



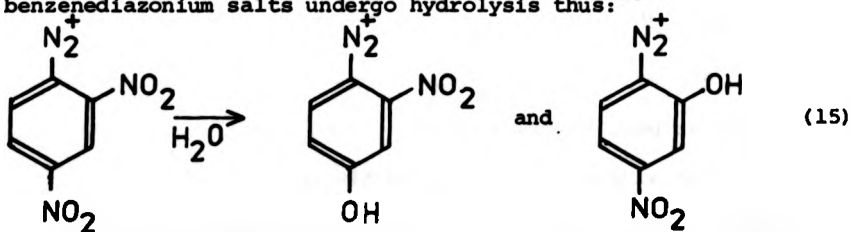
(14)

Arenediazonium salts are capable of forming metal complexes through the diazonium group, viz. (X).[46]



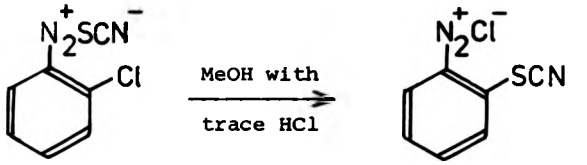
(X)

(iv) Reactions involving other ring substituents. The diazonium group is the most strongly electron-withdrawing group known[7] and therefore has a pronounced effect on other ring substituents. For example, aqueous solutions of 2,4-dinitrobenzenediazonium salts undergo hydrolysis thus:[56]



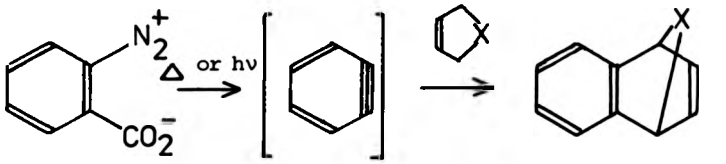
(15)

Certain arenediazonium salts undergo an inexplicable, irreversible exchange between their anions and ring substituents,[46] e.g.



(16)

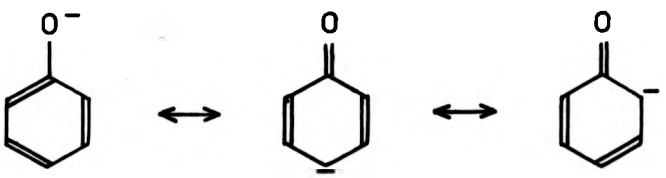
(v) Of great synthetic value is their capability of forming an aryne intermediate,[46] e.g.



(17)

1.3 The coupling reaction

The coupling reaction has been known since Griess first prepared Aniline Yellow in 1863.[57] Arenediazonium salts couple with a wide variety of compounds which include mono- and poly-hydroxyaromatics, aromatic amines, amides and heterocyclic compounds.[58] The requirement for coupling is an activated, electron-rich atom in the coupler which bonds to an electron-deficient diazonium group. For example, $-O^-$ activates the aromatic ring of phenol thus:[59]



(18)

facilitating coupling at the 2- and 4-positions to the corresponding azo-compounds. Those couplers used in the dyeline process (Section 1.7) should be colourless, stable to u.v. light and have the requisite reactivity. The azo dye produced must be strongly coloured, stable to light and insoluble in water. There is some preference for blue and black colours with paper-based products, although a variety of colours are produced commercially.

From a study of the coupling of arenediazonium salts with acids, Conant and Peterson[64] showed that the rates of coupling were proportional to the hydroxyl ion concentration up to ca. pH 9. They observed that k_{sl} (stoichiometric rate constant, see p.17) was affected by an acid-base equilibrium in one of the two reactants, which they suggested was the arenediazonium ion in equilibrium with the aryl diazohydroxide ($Ar-N=N-OH$). They proposed a factorisation of the observed rate constant as follows:-

$$\log k_s = \log k_o + pH \qquad (20)$$

where k_o is the rate constant at pH 0.

Wistar and Bartlett[66] pointed out that both the arenediazonium ion and the coupling component are subject to acid-base equilibria, viz.

Arenediazonium ion $Ar-N_2^+ + OH^- \rightleftharpoons Ar-N_2-OH$ (21)

Phenol $ArOH \rightleftharpoons ArO^- + H^+$ (22)

Amine $ArNH_3^+ \rightleftharpoons ArNH_2 + H^+$ (23)

Consequently, coupling can proceed by any of four different mechanisms. Their results indicate that the amine couples as follows:-

$$RNH_2 + ArN_2^+ \longrightarrow ArN_2RNH_2 + H^+ \qquad (24)$$

Putter's[71] results indicated, contrary to Conant and Peterson,[64] that phenols react as the phenolate ion, thus:

$$RO^- + ArN_2^+ \longrightarrow ArN_2OR \qquad (25)$$

1.3.1 Kinetics of the coupling reaction

There are a number of reviews on the coupling reaction, notably by Zollinger,[59] Müller, Putter[6] and Schudehütte[60] (in Houben Weyl), Radu[61] and Wulfman.[46]

First investigated in 1870, the coupling reaction has been studied by two main methods,[62] namely polarography, in which the decrease of the arenediazonium ion is followed,[63] and

colorimetry, in which the increase in the azo dye concentration is measured.[64-69] In 1897, Goldschmidt[58] determined the coupling reaction to be second-order according to (19).

$$\frac{d[Az]}{dt} = k_s [D][C] \qquad (19)$$

where

$[Az]$ = azo dye concentration; $[C]$ = coupler concentration

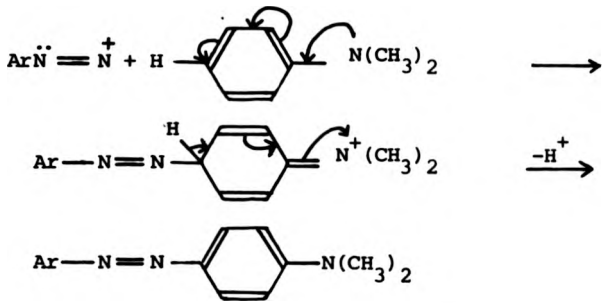
$[D]$ = arenediazonium ion concentration;

k_s = rate constant for stoicheiometric amounts of coupler and arenediazonium ion.

He deduced this from a study of the pH dependence of the rate constants for this reaction in a pH range above and below the pH corresponding to the pK_A values of the coupling components. The coupling rate constant depends on pH in two ways: below the pK_A of the coupler (where it is only partly ionised), the rate of reaction increases 10-fold per unit rise in pH, whereas above pK_A (where it is fully ionised), the rate constant is independent of pH.

Hauser and Breslow[72] and Zollinger[73] have rationalised the coupling reaction in terms of an electrophilic aromatic substitution involving activation of the ring by mesomeric release of electrons in the transition state. The ArN_2^+ entity has a strong electron-deficient nitrogen atom (bearing only six electrons) which confers on it a marked electrophilic character.

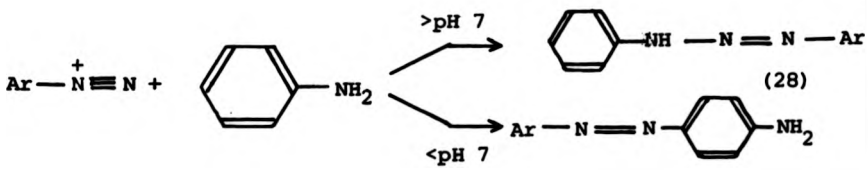
$$ArN^+ \equiv N \longleftrightarrow ArN^{\cdot\cdot} = N^+ \qquad (26)$$



(27)

For the coupling reaction with amines, $ArNH_2$ is the only conceivable reactive form. Theoretically phenols can react either as ArOH or ArO^-; however, the ionised form is far more reactive, as expected from the ability of $-O^-$ to transfer electrons into the ring as in (18).[58]

With primary amines, arenediazonium salts couple either to an active carbon atom or to the nitrogen of the amino-group. This depends both on ring substituents on the amine and on the pH.[60]



(28)

The N-coupled product isomerises to the C-coupled form on addition of acid.[60]

The phenolate ion can be regarded as reacting with the arenediazonium cation as follows:-

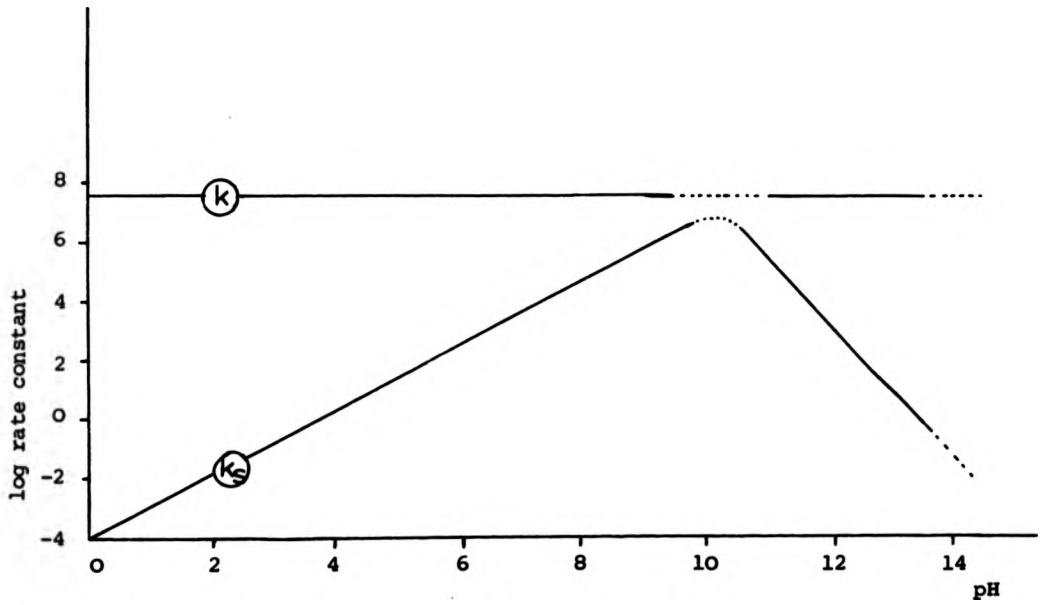
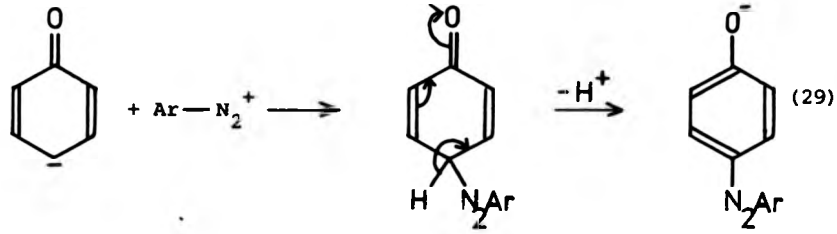


Figure 2 pH-Dependence on the rate constants of coupling 3-diazobenzene sulphonic acid with 2-naphthol-6-sulphonic acid

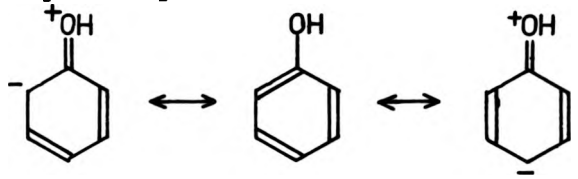
k = rate constant from equation 32

k_s = stoicheoimetric rate constant from equation 19



(29)

Zollinger[74] showed that coupling does take place with unionised phenols from observations of coupling in 60% sulphuric acid. The rate constant was found to be 10^{10} times less than that of coupling with the phenolate ion. The weak reactivity of phenol is presumably due to the contributions:



(30)

The ionic charges of the reactants in the coupling reaction between 2-naphthylamine-6-sulphonic acid and three arenediazonium salts were determined kinetically from the Brönsted-Bjerrum relation[75] by Zollinger,[76] who was able to show that it is the arenediazonium cation which couples to amines. Zollinger has since shown that it is the arenediazonium cation which reacts with the phenolate ion, again from the dependence of the coupling rate on the ionic strength,[77] and also from the observed base catalysis with pyridine.[78]

For coupling with certain arenediazonium cations in the pH range above the pK of the coupler, the rate of coupling decreases by a factor of 100 per unit rise in pH. This is due to the reaction of ArN_2^+ with hydroxyl ions via a metastable intermediate, the aryldiazohydroxide, to give the aryldiazotate (see Section 1.4).[68] As a result of this process, and also the established base-catalysed coupling in the lower pH range, an optimum rate is found (Fig. 2).[68]

Zollinger amended Goldschmidt's original kinetic equation (19) to:-[62,68]

$$\frac{d[Az]}{dt} = k\left[Ar—N_2^+\right]\left[RNH_2\right] \quad (31)$$

and $$\frac{d[Az]}{dt} = k'\left[Ar—N_2^+\right]\left[RO^-\right] \quad (32)$$

where k and k' are the 'absolute' coupling rate constants.

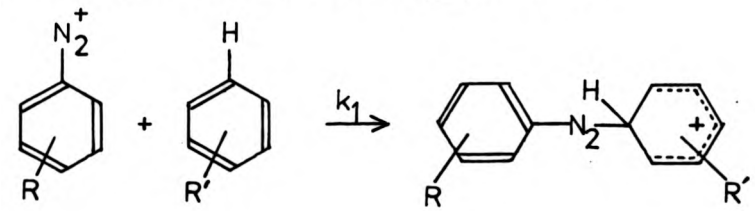
$\left[Ar—N_2^+\right]$ = concentration of arenediazonium salt,

$\left[RNH_2\right]$ = concentration of aromatic amine,

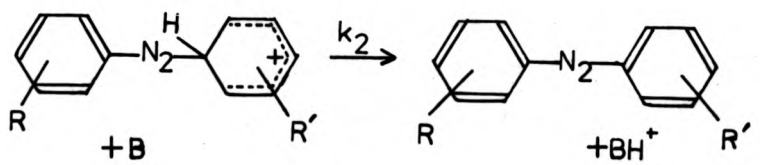
$\left[RO^-\right]$ = concentration of ionised (phenolic) coupler.

1.3.2 Mechanism of the coupling reaction

The coupling reaction is thought to be an electrophilic substitution reaction proceeding via two steps:[59]



(33)



(34)

The rate of coupling is not usually affected by the concentration of base B,[68,78] thereby excluding consideration of a transition state ($X^+ \cdots Ar \cdots H \cdots B$). Normally (33) is the rate determining step as there is no kinetic isotope effect. However, Zollinger[78] found that the coupling of arenediazonium salts with 2-naphthol-6,8-disulphonic acid and its 1-deuteriated analogue has a kinetic isotope effect of $k_H/k_D = 6.55$, which corresponds to the value expected with (34) as the rate-determining step.

He also found that this particular reaction is catalysed by bases such as pyridine, unlike coupling reactions with no demonstrable isotope effect. Zollinger incorporated the suggestion of the reversibility of step (33)[71] into the overall scheme, which involves a steady-state intermediate. Thus (33) becomes

$$Ar—N_2^+ + Ar—H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar—N_2—Ar^+—H \qquad (35)$$

A steady-state treatment of (34) and (35)[78] shows that the isotope effect depends on k_2, k_{-1} and $[\bar{B}]$ (the concentration of base), viz.

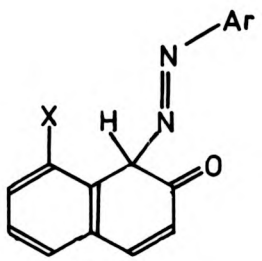
$$\frac{d[Ar\text{-}N_2\text{-}Ar]}{dt} = \frac{k_1 k_2 [B]/k_{-1}}{1+[k_2[B]/k_{-1}]} [ArH][ArN_2^+] \qquad (36)$$

If k_{-1} is very small, the rate becomes independent of k_2 and $[B]$, i.e. the expression reduces to

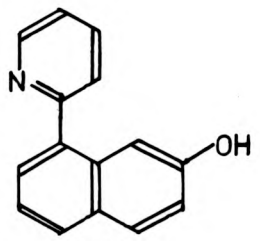
$$\text{Rate} = k_1[Ar - H][Ar - N_2^+] \qquad (37)$$

Under these conditions ($k_2 >> k_{-1}$), no base catalysis or isotope effect are expected. If,however, k_{-1} is large, both an isotope effect and base catalysis are found. Intermediate values of k_H/k_D have been found,[79] e.g. a value of 3.1 was calculated from the coupling reaction between arenediazonium cations and 1-naphthol-3-sulphonic acid (due to the steric effect of the sulphonate group in enhancing k_{-1}). k_{-1} is increased whenever the coupling site on the coupler is sterically hindered to attack by the arenediazonium cation.

Zollinger studied the kinetics of coupling of the diazobenzene-4-sulphonate cation with nine derivatives of 2-naphthol, substituted in the 8-position.[80] He obtained a Hammett plot for the X-substituted couplers, indicating that the steady-state intermediate (XI) exists.



(XI)



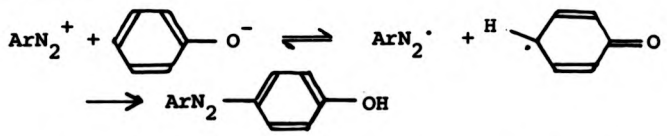
(XII)

Whilst a kinetic isotope effect of 2.7 was obtained with X = C_6H_5, with (XII) a value of only 0.9 was found, suggesting an intramolecular base catalysis by the pyridyl ring.

In 1968, Bubnov[81] proposed that the first step in nucleophilic and electrophilic substitution is an electron transfer, viz.

$$A^+ + B^- \longrightarrow A^\cdot + B^\cdot \longrightarrow AB \qquad (38)$$

In particular, he showed[82] from the observation of CIDNP of the ^{15}N nucleus that the coupling reaction between the benzenediazonium cation and phenol in basic methanol proceeds as follows:-



(39)

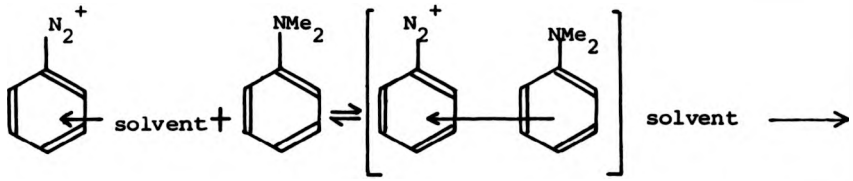
Zollinger[83,84] identified by u.v. and n.m.r. spectroscopy the steady-state intermediate in coupling reactions between three arenediazonium salts and six hydroxynaphthalene couplers. The results indicate that the intermediate exists as a charge-transfer π-complex, such as (XI).

Further examination of the coupling reaction has been conducted in non-aqueous media both by Zollinger[85] and more recently by Russian workers.[86-89]

Penton and Zollinger[85] determined the coupling rates of the reaction of dimethylaniline with 4-methylbenzenediazonium salts in four solvents, and found a variation in rate by only a

factor of 5. This infers both that solvation of arenediazonium ions and the interaction in the ion pairs are weak.

Bagal[86] used a range of solvents differing in donating characteristics and found a much larger variation in rate, and thus concluded that the arenediazonium ion is quite strongly solvated. He proposed a mechanism for the coupling of arenediazonium salts to dimethylaniline as follows:-



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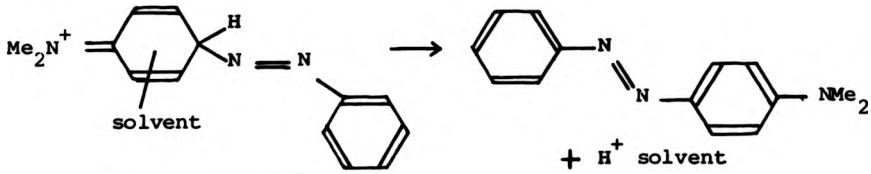
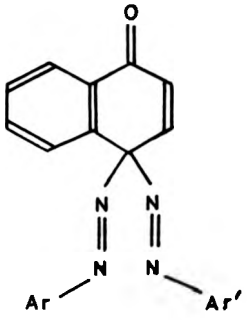


He also has shown,[87] by comparison of the coupling reactions between benzenediazonium salts and three aromatic amines which couple by the normal C-coupling with two which couple by N-coupling, in three solvents, that both the coupling component and the solvent act as catalysts by general base catalysis.

Hydrogen is not the only substituent that can be replaced in the coupling reaction: indeed, any substituent able to provide an electrophilic moiety can be replaced, e.g. SO_3^- as SO_3, COO^- as CO_2,[88] halogens[58] and activated methylene groups[89] such as CH_2OH,[90] but not usually alkyl groups.[91,91a]

A reactive arenediazonium ion can even replace a less reactive azo group,[92] the reaction proceeding via a metastable intermediate (XIII), e.g.



(XIII)

1.3.3 The effect of substituents on the coupling component

In order to give some rough prediction of the rate of coupling, Conant and Peterson [64] assigned 'B' values to couplers and 'A' values to ArN_2^+ where A + B = pH at which log k_s = 1. Another method is to incorporate the coupler pK values [71,68,93]. However, these methods give only a qualitative impression as there are a number of factors which govern the rate of coupling.

Electron-withdrawing substituents, such as sulphonate groups, reduce coupling ability, whilst electron-donating substituents, such as $-O^-$ groups, increase it, e.g. resorcinol couples much faster than phenol [69]. The increased substitution of 2-naphthol by sulphonate groups demonstrates their effect on the 'B' values [64], pK values [60] and rate constants, k, [71,73] for their coupling reaction with 4-morpholinobenzenediazonium salts (see Table 3).

Table 3

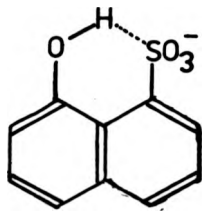
Effect on 'B' values, pK and log k (see above) of substitution of 2-naphthol by sulphonate groups

Coupler	'B' value[64]	pK[68]	log k[71,73]
2-naphthol	3.05	9.91	3.76
2-naphthol-6-sulphonic acid	3.62	8.94	2.35
2-naphthol-3,6-disulphonic acid	4.41	9.44	2.06

Sulphonate groups [94] reduce the rate of coupling by both steric and electronic effects. The 3-sulphonate group (in Table 3) has little effect on the acidity of the -OH group, unlike the

6-sulphonate group which increases the molecular dipole moment and hence the acidity of the hydroxyl group. The 3-sulphonate group acts primarily by a steric effect.

Putter[71] found that 1-hydroxynaphthalene-8-sulphonic and -2-sulphonic acids couple to ArN_2^+ faster than 1-naphthol compounds with a sulphonate group in other positions. This is due to hydrogen bonding from the hydroxyl group to the sulphonate group.



1-Naphthol-3-sulphonic acid couples exceptionally slowly because of the steric effect of the sulphonate group.

The presence of a second hydroxyl group in some couplers can induce production of bis-azo compounds (a good example is resorcinol[68]). This is not always the case and its prevalence depends on the conditions. Dihydroxy compounds can usually be considered to function as monohydroxy compounds up to pH values equivalent to pK_1 as only one hydroxyl group is ionised, pK_2 being often much higher.[93] Coupling usually takes place with dihydroxynaphthalene compounds in the ring with the more acidic hydroxyl group, e.g. in 1,8-dihydroxynaphthalene-4-sulphonate, coupling occurs in the 2-position, (moreover,a chelate ring is produced due to hydrogen bonding), viz.

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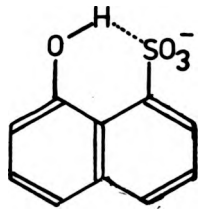

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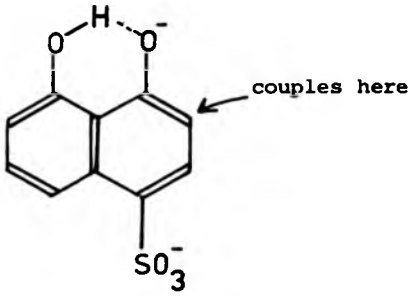
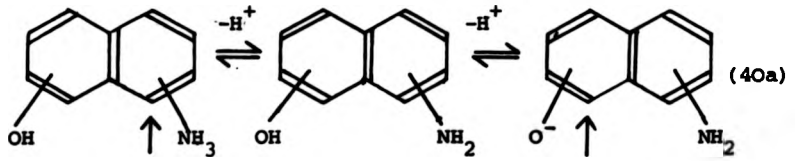


(XIV)

With 2,8-dihydroxynaphthalene-6-sulphonate,[93] coupling takes place in the 1-position, i.e. in the ring with the less acidic hydroxyl group, because of the steric effect of the sulphonate group.

The position of coupling in naphthalene compounds with a hydroxyl group in one ring and an amino group in the other depends on the pH. This is explained[68] kinetically by the effect of the proton concentration on the coupler, i.e.



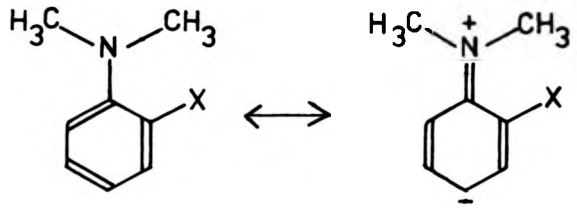
(40a)

couples here in acid couples here in base

The effect of pH on 2-amino-5-naphthol-7-sulphonate indicates that coupling occurs solely adjacent to the amino group at pH < 3.5 and solely adjacent to the hydroxyl group at pH > 6.5 (and at both positions in the intermediate range).[70]

The difficulty of coupling with 2-substituted N,N-dimethylaniline[95] is due to steric hindrance by the substituent X, to

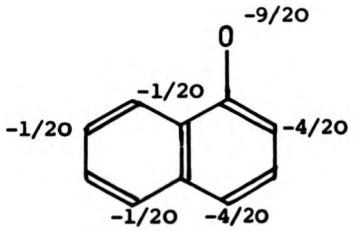
formation of the quinoidal form in (41)



(41)

Difficulty in coupling to the 4-substituted compound is due to steric hindrance in the 2-substituted intermediate by an N-methyl group.

Calculations[96] of electronic charge on the ring atoms of 1- and 2-naphthols rationalises why 1-naphthol couples in the 2- and 4-positions and 2-naphthol couples only in the 1-position.



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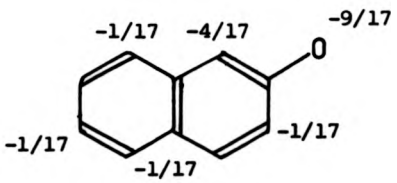


(XVI)

1.3.4 The effect of substituents on ArN_2^+

The effect of substituents can be demonstrated by the use of a Hammett plot, according to the equation[97]

$$\log k - \log k_o = \rho \sigma \qquad (42)$$

k = rate constant of substituted arenediazonium ion

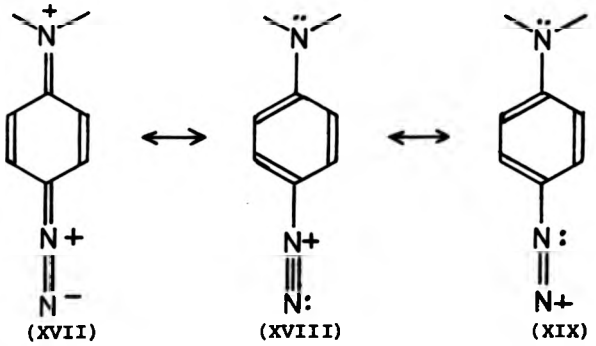
k_o = rate constant of unsubstituted arenediazonium ion

ρ = reaction constant

σ = substituent constant

By coupling substituted arenediazonium cations with hydroxynaphthalene compounds, both Zollinger[98] and ourselves[99] have proved the validity of this approach.

4-Amino substituents reduce the coupling ability of arenediazonium salts because of contributions from resonance structures of the type (XVII).[9]



(XVII) (XVIII) (XIX) (43)

The morpholino-substituted arenediazonium cation is more reactive than its N,N-dimethylamino analogue because the latter substituent can rotate freely to give the planar structure (XVII), whereas the morpholino group cannot as readily adopt the requisite planar configuration, being a puckered ring system.[59]

2- and 4-alkoxyl groups reduce the coupling ability of arenediazonium salts by mesomeric electron release into the ring, 3-alkoxyl groups activate ArN_2^+ by inductive withdrawal.[9,59] 2,5-diethoxy-4-morpholinobenzenediazonium cations have a slightly higher coupling ability than the 4-morpholino compound because the activating effect of the 5-ethoxy group is greater than the deactivating effect of the 2-ethoxy group.

Halogen and nitro-groups increase coupling ability due to increase of the electrophilic character of ArN_2^+. Substituent effects are usually additive,[100] although there are exceptions.[101] More recently, it has been found[102] that for highly activated arenediazonium cations, the substituent effects are only

approximately additive, becoming less so for those reactions, with rates of coupling approaching diffusion-control.

1.3.5 The 2-/4-ratio in coupled products

Many couplers, such as phenol, are able to couple in more than one position. Phenol normally couples in the 4-position, but with excess arenediazonium salt, also in both the 2- and 6-positions to give bis- and tris-azo compounds.[103] The ratio of the percentages of coupling in the 2-position and 4-position is known as the 2-/4-ratio and has been found to depend on several factors, namely:

(i) nature of the ArN_2^+;

(ii) solvent;

(iii) pH;

(iv) temperature;

(v) catalysis;

(vi) position of substituents in the coupler.

These factors have been extensively studied with 1-naphthol and its sulphonate derivatives. Discussing these factors in turn,

(i) investigations by Gattermann et al.[105] into the coupling of 1-hydroxynaphthalene-3- and 5-sulphonic acids with substituted arenediazonium salts showed that the 2-/4-ratio depends on the reactivity of the substituents. With 1-naphthol, it has been found that ArN_2^+ with electron-donating groups reduce coupling at the 2-position, whilst electron-accepting groups facilitate it.[106]

(ii) Bamberger found that in aqueous solution 98% of coupling occurs in the 4-position. In 85% ethanol, 22% of coupling occurs in the 2-position, whilst in benzene this figure rises to 90%.[107]

(iii) The effect of pH on the 2-/4-ratio is discussed by

Zollinger [104], who attributes the ratio largely to steric effects. The coupling of ArN_2^+ with 1-naphthol yields relatively more 2-coupled products at high pH [108] (Table 4).

Table 4

Percentage composition of the product from the reaction of benzenediazonium ions with 1-naphthol

pH	% product coupled at 4-position	% product coupled at 2-position	% product coupled at both 2- and 4-positions
5.7	98.5	ca. 1.5	ca. 0
7	86	5.4	8.6
9	68	15.1	16.9
12	42.6	27.4	29

The coupling of 2- and 4-diazophenols to 1-naphthol is strongly influenced by pH: at high pH, the diazophenolate ion couples principally at the 2-position, whilst at lower pH, when the compound is in the phenolic form, coupling takes place at the 4-position [104].

(iv) The 2-/4-ratio for the coupling between 1-naphthol-3-sulphonic acid and 2-nitrobenzenediazonium ions increases with increase in temperature [109].

(v) Apart from pH effects, increased concentation of the buffer gives more of the product coupled in the 4-position due to general base catalysis [109].

An isotope effect is found in the coupling of 4-chloro-benzenediazonium cations with 2-naphthol-6,8-disulphonic acid. The 2-/4-ratio.. is larger for the deuteriated compound than the protio form; thus at pH 4.6:

2-/4-ratio for deuteriated compound = 5.5

2-/4-ratio for protio compound = 6.3

This is because coupling at the 4-position is more strongly base-catalysed than that at the 2-position, and so the isotope

effect for coupling at the 4-position is also larger.

(vi) Gattermann *et al.*[105] demonstrated that 1,3- and 1,5-naphthylaminosulphonic acids have a greater tendency to coupling in the 2-position than the corresponding naphthols. Also 1,5-naphtholsulphonic acid has a greater tendency to couple in the 4-position than the 1,3-compound.

These various factors (i) - (vi) have been found to affect many other couplers, *e.g.* the 2-/4-ratio for the coupling of 1-naphthylamine with ArN_2^+ increases both with a rise in pH and on the addition of catalysts such as glycerine.[110]

1.3.6 Kinetics of coupling with bifunctional compounds

A technically important class of coupling reactions concerns the cases where either (or both) arenediazonium cation or coupler bears more than one reactive group.

The coupling rate of resorcinol increases more than 10 times per unit rise in pH.[64] This is because a solution of resorcinol contains one neutral and two ionised species, *i.e.* R^{2-}, RH^- and RH_2, each of which has a different coupling rate;[68] for example, R^{2-} couples 10^4 times faster than RH^-.

The pH of reaction and the concentration of buffers and additives have been found to affect the site of coupling, due to general base catalysis. For example, the addition of pyridine to the coupling of ArN_2^+ to resorcinol favours the 4,6-coupled product over the 2,4-compound. More recent work on resorcinol to further clarify the effect of pH has been published,[111] which indicates a rather complex picture.

Tetrazotized benzidine reacts in two stages and can couple sequentially to two different couplers.[112] The first arenediazonium group couples very rapidly because of the effect of the

other strongly activating diazonium group (σ = 1.8 [7]). The remaining diazonium group is activated only by the phenylazo residue (σ = 0.46), and thus coupling is enhanced to a lesser extent.[113]

Certain amino-hydroxynaphthalene compounds, e.g. 6-amino-1-hydroxynaphthalene-3-sulphonic acid,[114] will couple in both rings only if coupling occurs first in the ring bearing the amino group. In another group of this type, e.g. 7-amino-1-naphthol-3-sulphonic acid,[115] coupling occurs in both rings only if ArN_2^+ couples to the hydroxyl bearing ring first.

The formation of bis-azo-compounds[116] from 4-phenylenebis-diazonium salt with 2-naphthol-3,6-disulphonic acid is first-order with respect to the coupler, but of only fractional (0.65) order with respect to the arenediazonium ion. This is due to aggregation of the arenediazonium salt to dimers and oligomers, which can be broken up on the addition of urea. This also increases the rate both by base catalysis and dielectric medium effects.

1.4 The reaction of arenediazonium ion with base

Griess discovered that aqueous benzenediazonium salts give potassium benzene-syn-diazotates with aqueous KOH.[117] In 1894, Schraube and Schmidt[118] found that the syn-diazotate rearranges into the anti-isomer. The complex equilibria involved have been investigated by a number of groups and the reactions (44) to (49) are now generally accepted.[119-121]

$$ArN_2^+ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underline{syn}\text{-}ArN_2OH \qquad K_1 = k_1/k_{-1} \qquad (44)$$

(diazohydroxide)

$$\underline{syn}\text{-}ArN_2OH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underline{syn}\text{-}ArN_2O^- + H^+ \qquad K_2 = k_2/k_{-2} \qquad (45)$$

(diazotate)

$$\underline{syn}\text{-}ArN_2O^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underline{anti}\text{-}ArN_2O^- \qquad K_3 = k_3/k_{-3} \qquad (46)$$

$$ArN_2^+ + OH^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \underline{anti}\text{-}ArN_2OH \qquad K_4 = k_4/k_{-4} \qquad (47)$$

$$\underline{anti}\text{-}ArN_2OH \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \underline{anti}\text{-}ArN_2O^- + H^+ \qquad K_5 = k_5/k_{-5} \qquad (48)$$

$$\underline{syn}\text{-}ArN_2OH \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \underline{anti}\text{-}ArN_2OH \qquad K_6 = k_6/k_{-6} \qquad (49)$$

It is also known that both the syn- and anti-diazohydroxide tautomerise to the nitrosamine, but to an unknown extent.[121]

Wittwer and Zollinger[122] showed that the diazotate is produced by a two-step reaction, and they discovered that the equilibrium constant for reaction (44) is much smaller than that for reaction (45), and so the diazohydroxide is present in a very small amount. Equations (44) and (45) can be rewritten as follows:-

$$ArN_2^+ + H_2O \rightleftharpoons \underline{syn}\text{-}ArN_2OH + H^+ \qquad K_{A1} \qquad (50)$$

$$\underline{syn}\text{-}ArN_2OH \rightleftharpoons \underline{syn}\text{-}ArN_2O^- + H^+ \qquad K_{A2} \qquad (51)$$

where $$K_{A1} = \frac{[ArN_2OH][H^+]}{[ArN_2^+][H_2O]}$$

$$K_{A2} = \frac{[ArN_2O^-][H^+]}{[ArN_2OH]}$$

and $$K_{A1}.K_{A2} = K = \frac{[Ar\text{-}N_2O^-][H^+]^2}{[ArN_2^+]} \qquad (52)$$

omitting $[H_2O]$ as it is constant.

Taking logs:

$$pK_{A1} + pK_{A2} = \log\left[ArN_2^+\right] - \log\left[ArN_2O^-\right] - 2\log\left[H^+\right]$$

$$\text{therefore } pK_{A1} + pK_{A2} = \log \frac{\left[ArN_2^+\right]}{\left[ArN_2O^-\right]} + 2pH$$

$$\text{and } pH = \frac{pK_{A1} + pK_{A2}}{2} + \frac{1}{2} \log \frac{\left[ArN_2O^-\right]}{\left[ArN_2^+\right]} \qquad (53)$$

From equation (53), when $\left[ArN_2O^-\right]$ equals $\left[ArN_2^+\right]$, pH = $(pK_{A1} + pK_{A2})/2$, sometimes called pH_m). These values have been calculated for a number of substituted arenediazonium ions and it has been shown that pH_m falls as the substituent constant σ increases. Above pH_m, the rate of coupling falls as more of the non-coupling diazotate is produced. A plot of log k_A (k_A = apparent rate of coupling) against pH has a gradient of -2, as $\left[ArN_2^+\right]$ depends on $\left[H^+\right]^2$ [127] (see Fig. 2).

Most of the rate constants k_1 to k_6 and k_{-1} to k_{-6} have been measured for at least a few arenediazonium ions.[123-129] On addition of base to an arenediazonium salt, first the syn-diazotate is produced and then, more slowly, this isomerises to the anti-form.[121] The syn-diazotate is formed very quickly indeed, e.g. for the 3-nitrobenzenediazonium ion, k_1 = 4.5×10^5 dm^3 mol^{-1} s^{-1},[8] and since $k_1 < k_2$, k_2 cannot be measured. The rate of isomerisation to the anti-diazotate, k_3, is usually slower than k_1, the rate depending on ring substituents,[125] e.g.

benzenediazotate $k_3 = 2 \times 10^{-6}$ s^{-1}

4-nitrobenzenediazotate $k_3 = 5.4 \times 10^{-2}$ s^{-1}

To complicate matters further, at high pH the arenediazonium ion is very unstable and decomposes to phenols.[121] The diazotate, although relatively more stable, undergoes decomposition both photochemically and thermally. LeFevre[128] discovered that

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benzenediazotate $k_3 = 2 \times 10^{-6}$ s^{-1}

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To complicate matters further, at high pH the arenediazonium ion is very unstable and decomposes to phenols.[121] The diazotate, although relatively more stable, undergoes decomposition both photochemically and thermally. LeFevre[128] discovered that

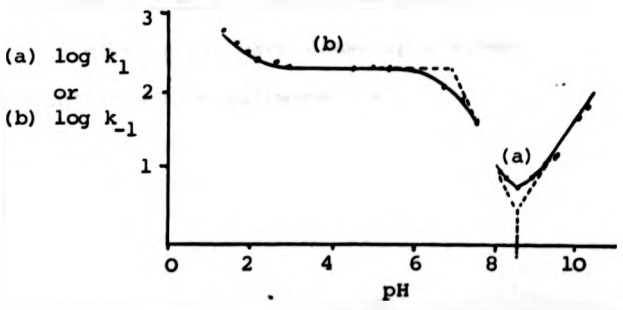
anti-aryldiazotates undergo first isomerisation to their syn-form and then decomposition under the action of u.v. light. He was not able to ascertain the nature of the products, however, except that they are not phenolic.

1.4.1 Arenediazonium ion $\rightleftharpoons$ syn-diazotate

The equilibrium arenediazonium ion $\rightleftharpoons$ syn-diazohydroxide $\rightleftharpoons$ syn-diazotate has been well investigated. k_1 and k_{-1} have been measured for a number of substituted compounds.[120,124,125,127,130], k_1 and k_{-1} being the rate-determining step of the forward and reverse reactions respectively. Equilibrium constants for the overall reaction may be calculated from (50) and (51) to give (52) Values for K_2 have been measured for some substituted arenediazonium ions, and from these the maximum concentrations of diazohydroxide, (i.e. at pH_m) have been calculated and found to be very low but increasing with increasing σ-values of the ring substituents,[22] e.g. with 3-NO_2-4-Cl as the substituent, at pH_m, % diazohydroxide = 2.05%. As for the coupling reaction, this equilibrium is also dependent on ionic strength.[129]

Both the forward and reverse reactions are pH-dependent. At ca. pH_m and higher, k_1 increases linearly with $[OH^-]$. Similarly, k_{-1} decreases linearly with $[H^+]$ and thus the apparent rate constant k_A has a minimum at pH_m (see Fig. 3).[121]

Figure 3 The pH-dependence of (a) log k_1 and (b) log k_{-1} of the forward and reverse reactions between 3-nitro-4-chlorobenzenediazonium ion and its corresponding syn-diazotate respectively



Values of k_1 are found to be lower than the rates of coupling with weaker bases such as the naphtholate ion.[131] This is because the OH^- ion is strongly solvated to water molecules and has to desolvate before reaction can occur. The N-O bond formation is relatively fast and not very selective, and thus ring substituents have a small effect on the rate of diazotate formation; thus, for this reaction, ρ is only 2.06.[131]

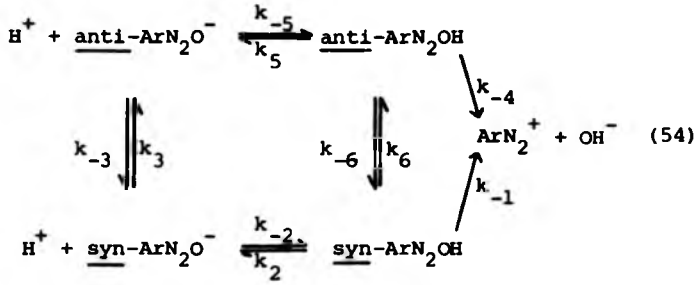
The reverse reaction at lower pH has been used to find k_{-1} and K_2.[129] Between ca. pH 2-5, most of the diazotate is rapidly converted to diazohydroxide first, and the subsequent formation of arenediazonium ion becomes pH independent. At even lower pH, k_A increases with increase in acidity (or concentration of acid buffers such as chloroacetic acid[120]) due to general acid-catalysis.[120,131]

Arenediazonium salts with strongly mesomeric groups give syn-aryldiazotates which isomerise relatively fast so that they exist essentially as steady-state intermediates, and so k_{-1} cannot be measured directly. With the most strongly mesomeric groups, such as 2,4-dinitro, it has been suggested[122] that $k_1 < k_3$.

1.4.2 Syn-anti isomerisation

Since the syn-anti isomerisations (46) and (49) are usually much slower than reactions (44) and (45), their kinetics can be studied quite separately.[119,120,123] The syn-diazohydroxide in alkaline solution is present in small concentration, and thus the forward step of (49) takes place to a very small extent.

Sterba et al. have drawn up a scheme for the various possible reaction pathways (54).



(54)

Rate constants k_3, k_{-3} and k_{-6} and equilibrium constants for reactions (46) and (48)[126,127] have been determined for a number of substituted compounds,

e.g. with 2-NO_2 as substituent, $k_3 = 1.5 \times 10^{-3}\ s^{-1}$

$k_{-3} = 8.3 \times 10^{-5}\ s^{-1}$

$k_{-6} = 1.9 \times 10^{-2}\ s^{-1}$

The reaction pathway from an anti-diazotate to the arenediazonium ion depends on the ring substituents and the pH. The dependence of log k_A (k_A = apparent rate constant) on pH is given in Fig. 4 for the benzenediazotate ion[123] and its 2-nitro-4-chloro-[127] and 2,4-dinitro-[120] derivatives.[121] Each of these three behaves differently and so will be dealt with separately.

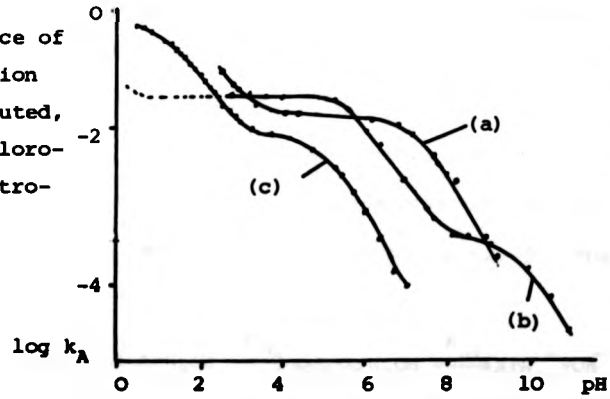
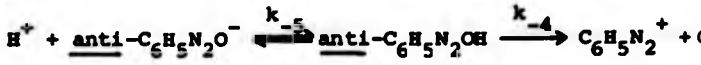


Figure 4 pH-dependence of log k_A of the conversion of (a) anti-unsubstituted, (b) anti-2-nitro-4-chloro- and (c) anti-2,4-dinitro-benzenediazotate into the corresponding arenediazonium cation

(i) Anti-syn isomerisation for benzenediazotate is very slow and so the main reaction pathway is via reactions (47) and (48), viz. (55):-



(55)

Above pH ca. 6, the overall rate is dependent on the $[H^+]$ and thus the rate limiting step is (48). Between pH 3 and pH 6, reaction (47) becomes the slower of the two and pH-independent. Above pH 3, reaction (47) becomes subject to acid-catalysis and so pH-dependent.[123,129]

(ii) Diazotates having ring-substituents with higher σ-constants such as 2-nitro-4-chloro-[126] behave differently because the splitting rate of diazohydroxide (k_{-4}) is less than in (i) and the isomerisation rate (k_{-3}) more, and as a result, different pathways are found. The splitting of the anti-diazohydroxide is much slower than either the isomerisation reaction or the splitting of syn-diazohydroxide, and so this becomes the main reaction pathway at high pH (56).

$$\underline{\text{anti}}\text{-ArN}_2\text{O}^- \underset{k_{-3}}{\rightleftharpoons} \underline{\text{syn}}\text{-ArN}_2\text{O}^- \underset{k_{-2}}{\overset{+H^+}{\rightleftharpoons}} \underline{\text{syn}}\text{-ArN}_2\text{OH} \xrightarrow{k_{-1}} \text{ArN}_2^+ + \text{OH}^- \quad (56)$$

The splitting of syn-diazohydroxide is the rate-determining step above ca. pH 9.5 and so becomes pH-dependent; thus a plot of log k_A vs. pH has a gradient of -1. At lower pH, the chemical flux increases and so the isomerisation(46) becomes the rate determining step and thus pH-independent. A plateau is not found as the various stages overlap. Below ca. pH 7.5, the concentration of anti-diazohydroxide becomes significant and its isomerisation becomes the rate determining step, hence the plateau below pH ca. 5. The pathway below pH 7.5 is

$$H^+ + \underline{\text{anti}}\text{-ArN}_2\text{O}^- \underset{k_{-5}}{\rightleftharpoons} \underline{\text{anti}}\text{-ArN}_2\text{OH} \xrightarrow{k_{-6}} \underline{\text{syn}}\text{-ArN}_2\text{OH} \xrightarrow{k_{-1}} \text{ArN}_2^+ + \text{OH}^- \quad (57)$$

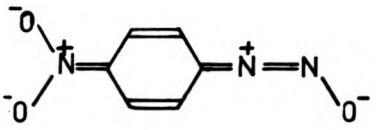
At low pH, the rate (k_A) increases further due to the acid-catalysed splitting of the anti-diazohydroxide.[129]

(iii) With still higher σ-values, the rate k_{-1} decreases further and the isomerisation rates k_{-3} and k_{-6} increase. The 2,4-dinitro

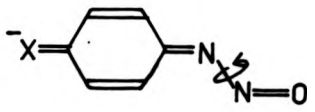
derivative, for example,[120] behaves as (ii) above pH 4.5 . It follows pathway (57) below pH 4.5; the non-catalytic splitting of syn-diazohydroxide (k_{-1}) has the slowest rate and is directly proportional to the anti-diazohydroxide concentration which is pH-dependent. At lower pH values, the proton-catalysed splitting of syn-diazohydroxide (k_{-1}) becomes more significant, until at pH 1 k_{-1} is greater than k_6, and so (49) becomes the rate-limiting step and the reaction pH independent.[120]

1.4.3 Conclusion

Littler[119] suggests two possible mechanisms for the syn-anti diazotate isomerisation. Those diazotates with strongly mesomeric groups such as 4-nitro involve a transition state (XX) whereas diazotates with less electron-withdrawing substituents isomerise by rotation about the N-N bond (XXI), which is a great deal slower.



(XX)



(XXI)

The syn-anti diazohydroxide isomerisation depends much less on the effect of ring substituents than the syn-anti diazotate isomerisation, and usually occurs at a higher rate. Plots of log k_1 and $2pH_m$ against σ fit the Hammett relationship well with ρ values of +2.61 and +6.58[132] respectively. (Other workers have found similar values.[13,129]) The latter value is due both to reactions (44) and (45), and is therefore a composite of both ρ values. Lewis and Suhr[129] found ρ values of 2.1 and 6.3 from the above plots, but, using σ_R^+ (see Section 1.5), Taft[133]

obtained better linearity with a ρ value of 6.56.

A relationship for the reverse reaction is more complicated as different pathways are found with different substituents. A value of ρ = -2.6 is found for a plot of σ against log k_{-4} when aryldiazotates with strongly electron-withdrawing substituents are omitted.[134]

1.4.4 Structure of diazotates

The debate on the structure of the different forms of aryldiazotates has a long and celebrated history, and the controversy as to whether the 'syn' or 'normal' form and the 'anti' or 'iso' form are geometrical or structural isomers has been described at length.[5,135] It is now universally accepted[121,137] that the two forms are indeed geometrical isomers. The assignment of the syn-form as cis and the anti-form as trans, originally predicted by Hantzsch,[137] has been based on analogy with similar compounds or on kinetic data. However, Sterba[130] found that isomerisation equilibrium constants of aryldiazotates with substituents in their 2-positions are strongly dependent on the substituent steric effect. This indicated that, in contrast to accepted opinion, the anti-diazotates in fact have the cis-configuration.

Infra-red data agrees with the previously accepted assignment of configuration and also shows that the N-N bond order exceeds that of the N-O bond. It predicts that anti-aryldiazotates are planar whereas the syn-isomers possess a non-planar distorted cis structure.[138]

Until recently,[139] no X-ray crystal structure of an aryldiazotate had been determined. Only one aliphatic diazotate[134,140] has been studied by X-ray methods and the syn-isomer was found to be cisoid, and therefore the anti-form is transoid. Potassium

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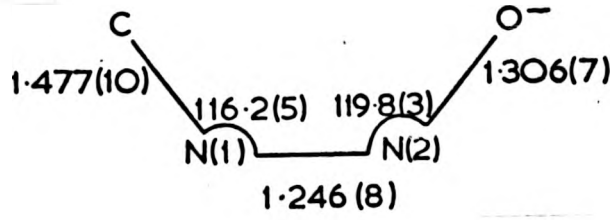
Until recently,[139] no X-ray crystal structure of an aryldiazotate had been determined. Only one aliphatic diazotate[134,140] has been studied by X-ray methods and the syn-isomer was found to be cisoid, and therefore the anti-form is transoid. Potassium

syn-methyl diazotate[141] has the structure (XXII).



(XXII)

1.5 Linear free energy relationships

Regularities in the effects of substituents on reaction rates and equilibria, mainly with aromatic compounds, were first noted in the mid 1930's.[142] Hammett[97] found that the log-log plot of the ionisation constants of substituted phenylacetic acids versus those of the corresponding benzoic acids is approximately linear (neglecting 2-substituents) and can be expressed as follows:-

$$\log (K_X)^{ArCH_2CO_2H} = \rho \log (K_X)^{ArCO_2H} + Y \qquad (58)$$

where K_X is the ionisation constant with a substituent X, ρ is the gradient and Y is the intercept. This treatment covers the case of hydrogen, i.e. the unsubstituted acids, enabling modification of (58) viz.

$$\log \left[\frac{K_X}{K_H}\right]^{ArCH_2CO_2H} = \rho \log \left[\frac{K_X}{K_H}\right]^{ArCO_2H} \qquad (59)$$

With the possibility of comparing any two of a large number of reactions with each other, Hammett chose the ionisation of benzoic acids in water at 25° C as the standard, when (59) becomes

$$\log \frac{K_X}{K_H} = \rho \log \left[\frac{K_X}{K_H}\right]^{ArCO_2H} \qquad (60)$$

$\log \left[\frac{K_X}{K_H}\right]^{ArCO_2H}$ has a fixed value for a particular substituent known as the Hammett substituent constant denoted σ, i.e.

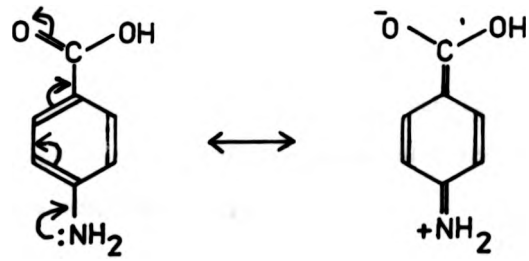
$$\log \frac{K_X}{K_H} = \rho \sigma \qquad (61)$$

An analogous equation is used for the correlation of rate constants.[142]

The gradient ρ, known as the reaction constant, depends on the nature of the reaction and is a measure of the susceptibility of the reaction or equilibrium to substituent effects.[143] A large ρ value implies a substantial change of charge at the atom of the reacting side chain attached to the benzene ring during the reaction. A positive ρ indicates that the reaction site increases in electron density during the reaction, and conversely a negative ρ indicates electron loss by the site. It has been found that a change of solvent or temperature may alter the value of ρ.[143]

Electron-withdrawing and donating substituents have positive and negative σ values respectively. Hammett found his σ-constants from the ionisation of substituted benzoic acids in water at 25° C but other values have been found under different conditions or from other reactions which fit eqn. (61).[144,145]

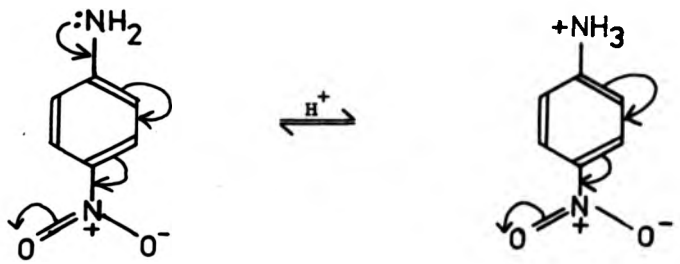
The function of the Hammett σ-constant is to give a value to the electronic interaction between the substituent and the ring. Substituents in 2-positions (ortho) are usually omitted as they often affect reactions sterically. Some substituents (e.g. NH_2-) in the 4-position conjugate directly with the carboxyl group of the benzoic acids by what is known as "through conjugation".



This effect gives σ-constants which are not solely due to their electronic interaction with the ring. In order to obtain a scale of σ-constants for reactions which do not involve through conjugation,

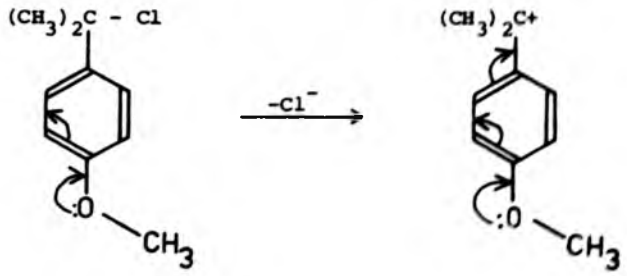
various workers have used other reactions such as the ionisation of phenylacetic acid[146] to obtain the values known as σ^{o}-constants. σ^{o} is the same as σ for all meta-substituents and those para-substituents which are not strong resonance donors.

There are two types of reaction in which through conjugation plays a major role and therefore modified σ-constants have been utilised. When the reaction centre is a strong electron donor, such as in the dissociation of the anilinium ion in water, substituents such as 4-nitro resonate with the non-ionised amino group but not with the ionised form, viz.[147]



(62)

From this reaction the series known as the σ^{-}-constants is obtained. The other type of constant has been found from reactions in which the reaction site is a strong electron acceptor and is known as σ^{+}.[148,149] The example of this type of reaction used to measure these constants is the S_N1 hydrolysis of phenyldimethylcarbinyl chloride in 90% aqueous acetone.[148] Those substituents with strong positive resonance contributions conjugate with the reaction site in only the ionised component, e.g.



(63)

Table 5[142,143] gives some examples of the above four types of substituent constant, the subscripts denoting the position of substitution.

Table 5

Selection of substituent constants

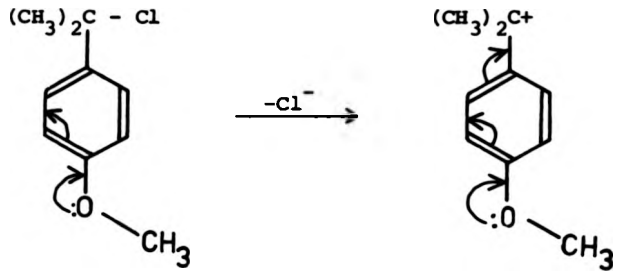
Substituent	σ_m	σ_p	σ_m^+	σ_p^+	σ_p^-	σ_p^o
H	0.00	0.00	0.00	0.00	0.00	0.00
NH_2	-0.16	-0.66	-0.16	-1.3	-0.66	-0.38
OCH_3	0.12	-0.27	0.05	-0.78	-0.27	-0.12
Cl	0.37	0.23	0.40	0.11	0.23	0.23
NO_2	0.71	0.78	0.67	0.79	1.27	0.78

In aromatic systems, para-substituent constants reflect both the resonance and inductive effects of the substituent group whereas σ_m -constants are mainly due to inductive effects. There is a small contribution, however, from resonance and so σ_m values are not quite the same as σ_m^+. Attempts have been made to separate resonance and inductive effects in order to include aliphatic systems and possibly other aromatic systems which do not fit eqn. (61) with any of the four substituent constants: σ, σ^o, σ^- or σ^+.

Since $\sigma_m \sim \sigma_I$ $(\sigma_m = \sigma_I + n\sigma_R)$ (64)

and $\sigma_p = \sigma_I + \sigma_R$ (65)

if σ_I could be found with sufficient accuracy, then from this σ_R values can also be determined. n is dependent on the particular



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Since $\sigma_m \sim \sigma_I$ $\quad (\sigma_m = \sigma_I + \alpha\sigma_R)$ (64)

and $\sigma_p = \sigma_I + \sigma_R$ (65)

if σ_I could be found with sufficient accuracy, then from this σ_R values can also be determined. α is dependent on the particular

substituent and describes the extent of resonance from the meta-position.[143] The reactions used to obtain values of σ_I utilise aliphatic systems with no resonance contributions. However, there are complications from large steric effects and these are accounted for by comparison of two similar reactions. Taft[146] utilised the acid and base hydrolysis of aliphatic esters with equation (66):

$$\sigma_I = \{\log (k_X/k_H)_B - \log (k_X/k_H)_A\} /1.12 \qquad (66)$$

The subscripts A and B denote acid and base hydrolysis respectively, and the factor of 1.12 is equivalent to a ρ value and puts σ_I on the same scale as the σ_m substituent constants which exhibit small resonance effects. This method is rather inaccurate due to certain incorrect assumptions; however, σ_I can be used for a variety of aliphatic systems. Equation (65) is used with σ_I to obtain a scale of σ_R values and also the constants σ_R^o, σ_R^- and σ_n^+.[143]

The substituent constants for a number of reaction systems do not fit exactly into the series σ, σ^+ or σ^- because of varying amounts of electron release by resonance: the Yukawa-Tsuno equation[150] attempts to account for this as follows:-

$$\log k_X/k_H = \rho \{\sigma + r (\sigma^- - \sigma)\} \qquad (67)$$

N.B. There is an analogous equation with σ^+ .

Values of r have been found to vary between over 1.2 and below 0.2 for a large number of reactions, but the usefulness of this equation in the study of other reactions is doubtful as r does not seem to correlate with ρ and so r is usually an unknown parameter.

Taft[133] has improved the accuracy of the values of σ_R, σ_R^o, σ_R^+ and σ_R^- by deriving average σ-constants from four groups of selected reactions, each group giving values of the substituent constants within known error limits. The equation used features two parameters:

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$$\log (k_X/k_H) = \sigma_I \rho_I + \sigma_R \rho_R \quad (68)$$

and has been found to fit a wide variety of reactions including the base hydrolysis of arenediazonium salts to aryldiazotates and the decomposition of arenediazonium salts in water, both using σ_R^+ constants in equation (68).

Many workers have tried to obtain a series of substituent constants for ortho-substituents with little success because, unlike para- and meta-substituents, they exert appreciable steric effects to a different extent for every reaction.[133,143] Using Taft's method[146] to find σ_I described above, a series of ortho-substituent constants (σ_o) based solely on their inductive effect has been made. In aromatic systems,[133] there are nearly as many series of σ_o constants as reactions examined. Table 6 lists the σ_o constants for 2-Cl and 2-NO_2 (used in this work) from a selection of reactions (for hydrogen, σ_o = 0.00).

Table 6

σ_o constants from a selection of reactions (from ref. 133 unless otherwise stated)

reaction	σ_o for 2-Cl	σ_o for 2-NO_2
Hydrolysis of aliphatic esters[146]	0.20	0.80
Ionisation of benzoic acids in n-butanol	1.08	1.78
Ionisation of benzoic acids in 73.5% aq. dioxan	0.84	1.58
Ionisation of *trans*-ArCH=$CHCO_2H$ in water	0.21	0.29
Ionisation of anilinium ion in water	1.95	4.86

With all of the substituent constants mentioned both here and elsewhere, such as Swain and Lupton's four-parameter equation[37] (see Section 1.2.5), the substituent effects in a large number of

reactions can be accounted for and much mechanistic information obtained. The subject of linear free energy relationship has been extensively described elsewhere, e.g. references 142, 143, 146, 151.

1.6 Flow techniques

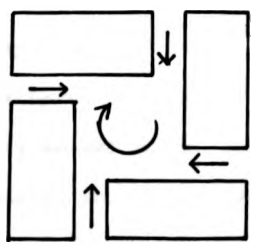
The rapid mixing of two reactant solutions and the subsequent monitoring of the reaction may be accomplished by various flow methods.[152-154] The first flow technique, developed in 1923, was the continuous flow method[155] in which two solutions are forced through a mixing device and subsequently along an observation tube. The extent of the reaction is observed at points along the tube, those more remote referring to later stages of the reaction. In this technique a wide variety of methods of observation are possible as there is no requirement for rapid observation techniques as with the accelerated and stopped flow methods. Slow observation techniques include the measurement of temperature along the tube and the conductivity of the solution, whereas fast techniques make use of u.v.-visible, n.m.r. and e.s.r. spectroscopy.[153] The advantages of this technique is that very short mixing times can be accomplished. The main disadvantage is that relatively large quantities of solvent and reactants are required. A variation is the accelerated flow method,[156] in which only small quantities of materials are required. A new accelerated flow apparatus is being developed for reactions with $t_{\frac{1}{2}} \sim 10^{-4}$ s^{-1}.[157] The rate of flow is adjusted,and so only one observation point, utilising a fast monitoring method, is needed.

In the continuous flow, and to a greater extent the accelerated flow methods, it is (incorrectly) assumed that the velocity of the reactant molecules in the observation tubes at the walls is the same

as that at the centre. These methods have been superseded by the intrinsically more accurate stopped-flow method which does not present this problem. The apparatus, first described by Roughton,[158] improved by Chance,[159] and finally perfected by Gibson,[160] is shown in Fig. 8, p. 70 . The reactants, after mixing, are initially forced down a tube and then the flow is suddenly stopped, either in a quartz cell, in which the absorbance is rapidly recorded, or in a nuclear magnetic resonance tube situated in a spectrometer cavity. An accuracy of between one and two per cent with a mixing time of ca. 5 ms can be obtained. Berger[161] used extra high pressures with a special stop syringe to achieve a mixing time of ca. 0.225 ms for reactions with $t_{\frac{1}{2}}$ ca. 0.5 ms. Various innovations and improvements have been introduced since the original design was made.[162,163] Caldin has described an apparatus for the study of reactions at temperatures down to -120° C. A more recent development is the incorporation of rapid scanning spectrometers (Section 2.3.3(ii)).

The design of the mixing device varies from a simple T-piece to more elaborate designs involving the use of usually four, but sometimes up to thirty, jets directed at each other and perpendicular to the direction of flow after mixing.[153,154,163]

Figure 5 Flow diagram of a four jet mixing device



Ott and Rys[165] found that with very fast reactions there is a product selectivity dependent on the diffusion rates of the reactants. As a result, by adjusting the mixing rate, different proportions of products may be obtained.

Finally, the quenching method,[160] a variation of which has been used both in the azo coupling reaction[70] and the study of aryldiazotates,[120] involves forcing the reactants through a mixing chamber, down a tube, into a solution of quenching reagent. In the study of aryl diazotates, a coupler solution is used to remove rapidly all of the arenediazonium cations. The products can be analysed at leisure,and reaction times down to 0.1 s can be achieved.

1.7 The dyeline process

The reaction of arenediazonium salts with couplers to produce azo dyes has been utilised in the dyeline process in which various methods have been developed (outlined below) to produce either a positive or negative image quickly and cheaply. The first commercially viable dyeline process was exploited by Kalle *et al.* in 1923, and the technique has remained basically unchanged since then.[167] The production of an image is accomplished in two steps. Finally, the photosensitive material (the arenediazonium salt) which is dispersed as a thin coating on the supporting paper or polymer film, is irradiated with near u.v. light (from a mercury lamp) through the diapositive. The diapositive, which is the image to be copied, is usually in the form of a tracing on transparent paper or film. In the second stage, the (positive) image is developed by coupling the remaining arenediazonium salt to a suitable coupler to achieve an easily perceptible image, preferably of black of blue-black hue, although many other colours may be produced.[168]

The ideal arenediazonium salt for the dyeline process is one

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which is both thermally stable and very sensitive to near u.v. light. With simple arenediazonium salts this is not achieved,and so appropriately modified compounds have been synthesised. They are usually 4-tertiaryamino-2,5-dialkoxybenzenediazonium salts, most often as the tetrafluoroborate or tetrachlorozincate salt[12,13] which are stable, pale yellow solids. The 4-substituent shifts the absorption wavelength to one corresponding to the emission maximum of the mercury u.v. lamp, whilst the 2-substituent increases the thermal stability of the compound and the 3-substituent broadens the absorption curve and moves the absorption maximum closer to the visible wavelength region (although it makes them slightly less stable). Arenediazonium salts of this type are fairly stable in the dark at room temperature and have a shelf life of over a year. Faster coupling may be obtained by the use of 4-tolylthio or 4-morpholino instead of 4-alkylamino-compounds, although this reduces shelf life.

The couplers[169] used are usually substituted naphthols or phenols, and the choice of coupler and arenediazonium salt governs the colour of the print. The pK_A of the coupler is important[94] and so the choice of coupler also depends on the development method used, i.e. in the semi-wet process, couplers which have low pK_A values are required, and in the ammonia process the pK_A of the coupler should be at least 10 in order to avoid precoupling before use.[169] Black images are not easily made but may be achieved by the use of two couplers competing for one arenediazonium salt, and they correspond to absorption by two azo dyes. Since the two couplers couple at different rates,the amount of each used has to be accurately calculated or even adjusted during a run: moreover, the pH has to be accurately controlled, but

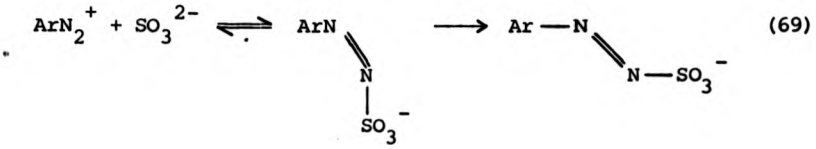
even so a perfect black is not always obtained.[94]

The development stage, in which the image is produced by the coupling reaction is accomplished by a number of methods. In the simplest (the so-called semi-wet process), the paper coating contains only the arenediazonium salt which is developed by the application of a freshly prepared solution of coupler.[58] The coupler solutions are rather unstable due to aerial oxidation. In the most commonly used process, known as the dry-development or ammonia process, the paper or polymer film coatings contain both arenediazonium salt and coupler, which are prevented from pre-coupling by keeping the pH as low as possible by the presence of a crystalline organic acid such as tartaric or citric acids. The image is developed by the use of ammonia vapour[58,168] which neutralizes the acid and increases the pH. The main disadvantage with this process is the unpleasant smell of ammonia, and to avoid this, other development techniques have been sought[12] including two which utilise heat to develop the image. In the first of them, inactive arenediazonium salts such as 'diazosulphonates' may be used which rearrange on heating to give the corresponding arenediazonium salt which couples at the pH of the paper. The 'diazosulphonate' chosen rearranges on exposure to light to a very light-sensitive arenediazonium salt which decomposes before it can couple. Heat treatment may be used to bring about a change in pH by the decomposition of some added substance. Urea is popular in this process as it is cheap; it operates by producing ammonia on heating. Often a heat-sensitive acid such as trichloroacetic acid[12] is added to prevent pre-coupling. The pH can be raised by the production of sodium hydroxide from the electrolysis of sodium chloride, which is added to the paper.[58]

Negative images[12] may be obtained by the use of paper film coatings which consist of an arenediazonium salt which couples with its own photodecomposition product. The most commonly used method is a variation on the 'diazosulphonate' coating described above. In this, the light does not immediately decompose the arenediazonium salt (produced by the action of light), and so this then couples to produce a negative copy.

A useful process in which a metallic print is obtained, which is exploited in the production of printed circuits, is the Philips process.[12] In this, the arenediazonium salt decomposition product (usually from a diazosulphonate) is used to reduce a metal salt (usually silver). The vesicular process[12] involves the formation of nitrogen bubbles from the photochemical decomposition of the arenediazonium salt in a transparent polymer film (e.g. P.V.C. or P.V.A.). The film then gives a positive image if viewed by reflected light, but a negative image with transmitted light. Lithographic plates[12] can be made by the use of an arenediazonium salt that gives an oleophilic product on exposure to light which can be used, after removal of the remaining arenediazonium salt, lacquering and inking, as a negative working plate. Positive images may be produced by a more recent method which involves the cationic polymerisation of cyclic ethers by the photodecomposition products from arene-diazonium salts. The remaining monomer (in the unilluminated regions) is washed away with a suitable solvent.[170] Positive-working plates can also be made by the use of a substance which produces an alkalie soluble product (usually a carboxylic acid) on exposure to U.V. light and is washed away, leaving the original oleophilic substance (e.g. naphthaquinone-1,2-diazide sulphonyl-amide) in the unexposed areas.[12]

The 'diazosulphonates' mentioned above are synthesised from arenediazonium salts with sulphite ions. As with aryldiazotates, there are two isomeric forms,[121] i.e.



(69)

Apart from the substances already mentioned, additives to the paper include:[12,58] (i) fluorescing agents which give the impression of increased contrast, (ii) stabilisers which form complexes with arenediazonium cations, such as with 2-nitroindan-1,3-dione, (iii) substances to increase the rate of bleaching and (iv) substances that absorb u.v. light thus reducing the contrast and so helping to give a continuous tone.

The paper itself is precoated with a substance such as silica to give it a smooth surface, thus preventing the reactants from sinking into it. When this happens, the arenediazonium salt is not completely bleached by the u.v. light, and not all the dye produced will be clearly visible.[12]

2. Materials and Methods

2.1 Materials

4-tolylthiobenzenediazonium tetrachlorozincate and many of the couplers were gifts from Transworld Reprographic Technology Ltd. (T.R.T.), Loughton, Essex. The other arenediazonium salts used in this work were prepared by the five methods described below (Sections 2.1.1 - 2.1.5). Apart from the methods in sections 2.1.8 - 2.1.11, the remaining couplers were purified by recrystallization from nitrogen-flushed water.

2.1.1 Preparation of 4-chlorobenzenediazonium tetrafluoroborate[5]

4-Chloroaniline (6.35 g, 0.05 mol) was dissolved in warm 10 M HCl (35 cm^3) and then cooled to ca. 0° C in ice. A solution of sodium nitrite (3.5 g, 0.05 mol in 10 cm^3 water) was then added dropwise to the rapidly stirred mixture maintained below 5°C. The resulting solution of 4-chlorobenzenediazonium chloride was filtered and the tetrafluoroborate salt precipitated with excess concentrated fluoroboric acid (20 cm^3). The white microcrystals were filtered by suction, washed with small portions of water and finally with ether. The product was dried in a vacuum desiccator over silica gel and stored in the dark at ca. -20° C. Yield 10.3 g (91.2%). The compound slowly decomposed on storage and after ca. 6 months had to be purified as follows: the salt was dissolved in a minimum of acetone, filtered, and reprecipitated on the addition of excess ether. The pure white solid was filtered, washed thoroughly with sodium-dried ether and dried as above. Yields of ca. 35-40% were obtained with a purity of over 99% (by microanalysis for C, H, N and Cl).

The following arenediazonium salts were also prepared by this method:-

benzenediazonium tetrafluoroborate,

2-chlorobenzenediazonium tetrafluoroborate,

3-chlorobenzenediazonium tetrafluoroborate,

4-methylbenzenediazonium tetrafluoroborate.

2.1.2 Preparation of 4-nitrobenzenediazonium tetrafluoroborate[5]

4-Nitroaniline (7 g, 0.05 mol) dissolved in 5 M HCl (45 cm^3) was cooled to 5° C with ice (70 g) and then aqueous sodium nitrite solution (3.5 g, 0.05 mol in 20 cm^3) was added. The mixture was stirred for ten minutes, filtered and then treated with concentrated fluoroboric acid (25 cm^3) to precipitate the product. The pale brown solid was filtered by suction, washed with ether, dried and stored by the same method as in section 2.1.1. Yield, 10.6 g (89.1%).

2.1.3 Preparation of 2-nitrobenzenediazonium tetrafluoroborate[5]

2-Nitroaniline (7 g, 0.01 mol) was made into a paste with water (14 cm^3) and sodium nitrite (3.7 g, 0.01 mol). The paste was mixed with ice (15 g) and while being cooled in ice, concentrated hydrochloric acid (15 cm^3) was added. The mixture was stirred for ten minutes and filtered, and fluoroboric acid (15 cm^3) gradually added to give pale yellow microcrystals of the product which were filtered, washed first with water and then with ether, dried in a vacuum desiccator over silica gel overnight and stored in the dark in a refrigerator (ca. -20° C). Yield, 4.0 g (33%).

The following arenediazonium tetrafluoroborate salts were also prepared by this method:-

4-cyanobenzenediazonium tetrafluoroborate,

2-nitro-4-chlorobenzenediazonium tetrafluoroborate,

2-chloro-4-nitrobenzenediazonium tetrafluoroborate.

2.1.4 Preparation of 2,4-dinitrobenzenediazonium tetrafluoroborate[5]

Dried sodium nitrite (3.5 g) was slowly added,with stirring, to concentrated sulphuric acid (75 cm^3), the temperature being kept

below 40° C, to give nitrosylsulphuric acid. 2,4-Dinitroaniline (8.3 g) was then slowly added with stirring at 30° - 35° C, and the mixture stirred for 3 hours. Ice (30 g) and then water (30 cm^3) were added to the mixture and then a saturated solution of sodium fluoroborate (70 cm^3) which slowly precipitated white crystals which proved not to be an arenediazonium salt. However, on addition of more water (40 cm^3), a thick yellow solid was deposited which was filtered, washed with further portions of water and then ether, dried and stored as described in section 2.1.1. This proved to be the desired product by u.v.-spectroscopy and azo dye forming properties. Yield, 8.4 g (65%).

2.1.5 Preparation of 4-phenylene-tetrazonium tetrafluoroborate[7]

Nitric acid (50 cm^3 of 50%) was added dropwise to arsenic(III) oxide (50 g) at 70° C on which a mixture of NO and NO_2 was evolved. These were combined to give N_2O_3 (10 cm^3) as a dark blue liquid, by cooling to -76° C in an acetone/dry ice slush bath.

Phenylene-diamine (1 g) in fluoroboric acid (5 cm^3) was cooled to -30° C with dry ice, and N_2O_3 (2 cm^3) added. The temperature was allowed to rise to 5° C and then a further portion of N_2O_3 (3 cm^3) was added to the mixture (at - 30° C), again allowing the temperature to rise to 5° C. The slurry was filtered through a sinter, washed with fairly concentrated fluoroboric acid (ca. 20%) and pumped to dryness in a vacuum desiccator. It was stored at -20° C in a refrigerator. Yield, 1.7 g (60.8%).

2.1.6 Preparation of crystalline disodium syn-benzenediazotate-4-sulphonate[170a]

The chloride salt of benzenediazonium-4-sulphonic acid was first made by the "inverted" method.[5] Sulphanilic acid (8.5 g) and sodium nitrite (3.5 g) were dissolved in water (60 cm^3) and the arenediazonium salt precipitated on the addition of concentrated

hydrochloric acid (5.5 cm^3). This was filtered and washed with water and the still damp product mixed with an equal weight of crushed ice, stirred and treated with 40% sodium hydroxide solution (80 cm^3). Colourless needles separated after 12 hours at 0^o C. These were filtered and washed with cold methanol. (Yield, 3.2g). The u.v. spectrum was found to be similar to that reported by Le Fevre et al.[170a] and furthermore slowly gave the anti-isomer. Microanalysis results were inconclusive but indicate the stoichiometry: $Na_2C_6H_4N_2O_4S.3H_2O$. This formulation was ultimately confirmed by X-ray crystal structure analysis.

2.1.7 Preparation of anti-4-nitrobenzenediazotate (potassium salt)[11]

A solution (20 cm^3) of 4-nitrobenzenediazonium chloride was prepared by the direct method (see section 2.1.2), mixed with 40% potassium hydroxide solution (50 cm^3) and the brown precipitate filtered and washed with water. Crystals were obtained by slow (over 24 hours) recrystallisation from methanol. The u.v. spectrum was the same as that obtained by Lewis and Hanson[123] and microanalysis gave the stoichiometry: $C_6H_4O_3N_3K.H_2O$.

Microanalysis results

Element	Theoretical	Found
Carbon	32.78%	32.31%
Hydrogen	2.71%	2.73%
Nitrogen	18.82%	18.76%

2.1.8 Purification of 2,7-dihydroxynaphthalene-3,6-disulphonic acid and 1,8-dihydroxynaphthalene-3,6-disulphonic acid[171]

The following procedure was used for both compounds.

The grey,impure material (ca. 4 g) was dissolved in 0.1 M hydrochloric acid (30 cm^3) which had previously been flushed with nitrogen for 20 minutes. This solution was boiled for 2 minutes with activated charcoal, filtered,and the product was isolated by

removing most of the solvent with a rotary evaporator, cooling, filtering off the pure white microcrystals and drying in vacuo over P_2O_5. The entire operation was carried out, and the product stored, in the dark. (Yield, ca. 2 g).

2.1.9 Purification of 2,3-dihydroxynaphthalene-metal complexes

The 2,3-dihydroxynaphthalene complexes with niobium(V), molybdenum(V) and tantalum(V) as supplied by T.R.T. were free from impurities except for some 2,3-dihydroxynaphthalene. Since this is soluble in hot petrol, whereas the complexes are not, the crude materials were boiled with petrol and filtered while still hot. This was repeated until no change in their i.r. spectra was observed.

2.1.10 Preparation of N,N-dimethylbenzamide[172]

Dimethylamine was passed over a rapidly stirred solution of benzoyl chloride (ca. 2 g) in petrol (75 cm^3) until no further white fumes were observed in the reaction vessel. Dimethylamine hydrochloride was filtered off, then half of the petrol removed by distillation under reduced pressure, and the product precipitated on cooling to 0° C in a refrigerator. The colourless needles were soluble in water, m.p. 40°-41° C, and the structure confirmed by its i.r. spectrum.

2.1.11 Preparation of 1,8-dihydroxynaphthalene[173]

Sodium 1-naphthol-8-sulphonate (7 g), potassium hydroxide (30 g) and water (10 cm^3) were heated to 220° C for 15 minutes and then allowed to cool. The product was mixed with 0.1 M hydrochloric acid (600 cm^3) and the 1,8-dihydroxynaphthelene filtered off. It was first recrystallised from hot water and secondly from a 40:60 mixture of benzene and petrol (40°-60° boiling range) to give a white crystalline material. M.p. = 140° C. Yield, 23%.

2.1.12 Preparation of 4-(4-chlorophenylazo)-1,8-dihydroxynaphthalene[6]

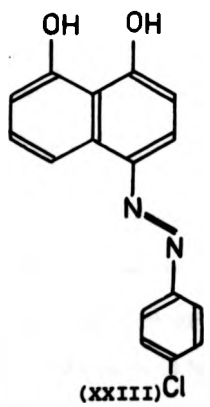
The coupling product from 1,8-dihydroxynaphthalene and 4-chlorobenzenediazonium salts has two absorption maxima in its visible spectrum, and in order to ascertain whether one or two dyes are produced, a quantity of material was prepared as follows:- 1,8-dihydroxynaphthalene (2 g) was dissolved in warm 0.1 M sodium hydroxide solution (50 cm^3) and 4-chlorobenzenediazonium tetrafluoroborate (0.5 g), in a minimum of water, was added slowly with stirring. The purple dye was filtered off, washed with cold water and dried. Yield, 0.4 g.

T.l.c. indicated that there is only one dye present, and microanalysis gave the stoichiometry $C_{16}H_{11}N_2O_2Cl$.

Microanalysis results

Element	Theoretical	Found
Carbon	64.32%	64.48%
Hydrogen	3.69%	3.82%
Nitrogen	9.38%	9.05%

This suggests the structure (XXIII).



(XXIII)

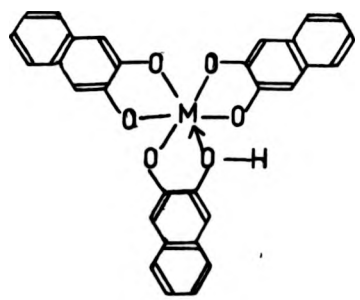
The u.v. spectrum showed two peaks (λ_{max} = 390 nm and 520 nm).

2.1.13 Preparation of 1-(4-chlorophenylazo)-2,3-dihydroxy-naphthalene-6-sulphonic acid

4-Chlorobenzenediazonium tetrafluoroborate (0.5 g) was dissolved in a minimum of water and added to an excess of sodium 2,3-dihydroxynaphthalene-6-sulphonate in aqueous solution. A few drops of aqueous sodium hydroxide were added to give a dark red solution from which the azo dye was precipitated with concentrated sodium chloride solution (ca. 10 cm^3). The precipitate was washed with slightly acidic water and then air-dried. The whole procedure was carried out, and the dye stored, in the dark to prevent decomposition. (Yield, 0.4 g).

2.1.14 Gravimetric analysis of 2,3-dihydroxynaphthalene-niobium complex[174]

Andra gives the structure for 2,3-dihydroxynaphthalene-metal complexes of Nb(V) and Ta(V) as:



M = Nb(v) or Ta(V)

(XXIV)

Microanalysis results were inconclusive and so to ascertain the purity of the Nb(V) complex, a gravimetric analysis was carried out. An accurately weighed sample of purified 2,3-hydroxynaphthalene-niobate (0.1316 g) was first gently, and then more strongly, heated to ca. 800° C in a platinum crucible (with lid) to a constant weight. After cooling, a few drops of concentrated nitric acid were added and the mixture reheated to

ensure complete conversion to Nb_2O_5. The results confirm the 1:3 complex with at least 99% purity.

Theoretical percentage of Nb 16.23%

Experimental percentage of Nb 16.17%

2.1.15 Gravimetric analysis of 2,3-dihydroxynaphthalene-molybdenum(V) complex[174]

An accurately known weighed sample was heated at 500° C in a platinum crucible to constant weight. The proportion of molybdenum was calculated assuming the product to be MoO_3 The result indicated a structure similar to (XXIV) with M = Mo.

Theoretical proportion of Mo in 1:3 complex = 16.67%

Experimental proportion of Mo in1:3 complex = 15.96%

Therefore purity = ca. 95%.

2.1.16 Analysis of the azo dye from the 2,3-dihydroxynaphthalene-niobium complex and 4-chlorobenzenediazonium tetrafluoroborate

To ascertain the structure of the azo dye obtained from the 2,3-dihydroxynaphthalene-niobium complex with 4-chlorobenzenediazonium tetrafluoroborate, it was first isolated and then analysed by conventional gravimetric[174] and also microanalysis.

(i) Isolation of dye

The coupler (1.0 g) was dissolved in a mixture of methanol and pH 11 buffer (1:1, 30 cm^3, see section 2.2), filtered and treated with aqueous 4-chlorobenzenediazonium tetrafluoroborate (0.3 g in 20 cm^3) to give a purple dye which precipitated out on addition of a concentrated solution of sodium chloride (ca. 10 cm^3). The dye was washed with water and dried in an oven.

(ii) Analyses[174]

The compound was expected to have a stoichiometry:

$Nb(C_6H_{10}O_2)_3N_2C_6H_4Cl$

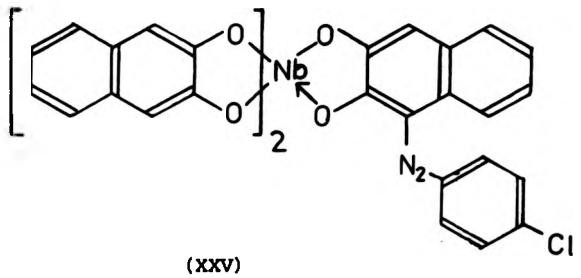
Microanalysis results

Element	Theoretical	Found
Carbon	61.14%	55.25%
Hydrogen	3.11%	3.38%
Nitrogen	3.96%	4.96%

These results are rather inconclusive, but from gravimetric analysis (see section 2.1.14 for method) we obtained the following:

Theoretical proportion of niobium	13.0%
Experimental proportion of niobium	13.17%

Thus the dye is taken to be



(XXV)

2.2 Buffer Solutions

A selection of typical buffer solutions used in this work are listed in Table 7.[175] Since the ionic strength of the solutions used in both the coupling reaction[76] and the equilibrium between diazonium ion and diazotate affects the rates of reaction, it was adjusted to μ = 0.25 moles dm^3 with a calculated amount of KCl. All the solutions were prepared from dried A.R. grade, solid materials and A.R. volumetric standard solutions of HCl and NaOH in doubly distilled water. The final pH after reaction was often found to differ slightly from the calculated value. Because of this, the pH after reaction was always measured with a PYE PW9410 pH meter with a glass electrode, accurate to ± 0.02 pH.

Table 7

Composition of buffer solutions

Composition	pH
0.1 M potassium hydrogen phthalate (50 cm^3) + 0.1 M HCl (22.3 cm^3) + KCl (0.83 g)	3.0
{Sodium acetate (1.361 g) + glacial acetic acid (0.6 g) + KCl (18.9 g)} dm^{-3}	4.6
{Sodium acetate (6.8 g) + glacial acetic acid (0.3 g) + KCl (14.9 g)} dm^{-3}	5.6
0.025 M borax (50 cm^3) + 0.1 M HCl (17.7 cm^3) + KCl (0.81 g)	6.1
0.1 M NaH_2PO_4 (50 cm^3) + 0.1 M NaOH (8.1 cm^3) + KCl (1.33 g)	6.2
{Na_2HPO_4 (1.79 g) + NaH_2PO_4 (1.56 g) + KCl (16.75 g)} dm^{-3}	6.4
0.1 M NaH_2PO_4 (50 cm^3) + 0.1 M NaOH (37 cm^3) + KCl (0.90 g)	7.3
0.1 M NaH_2PO_4 (50 cm^3) + 0.1 M NaOH (44.2 cm^3) + KCl (1.08 g)	7.6

Table 7 (continued)

Composition	pH
0.1 M NaH_2PO_4 (50 cm^3) + 0.1 M NaOH (46.7 cm^3) + KCl (1.11 g)	8.0
0.025 M borax (50 cm^3) + 0.1 M HCl (20.5 cm^3) + KCl (1.62 g)	8.0
0.025 M borax (50 cm^3) + 0.1 M HCl (16.6 cm^3) + KCl (0.81 g)	8.4
0.1 M $NH_2C(CH_2OH)_3$ (50 cm^3) + 0.1 M HCl (14.7 cm^3) + KCl (1.45 g)	8.5
0.025 M borax (50 cm^3) + 0.1 M NaOH (3.6 cm^3) + KCl (0.614 g)	9.25
0.025 M borax (50 cm^3) + 0.1 M NaOH (13.1 cm^3) + KCl (0.49 g)	9.6
0.05 M $NaHCO_3$ (50 cm^3) + 0.1 M NaOH (6.2 cm^3) + KCl (1.66 g)	9.7
0.05 M $NaHCO_3$ (50 cm^3) + 0.1 M NaOH (17.8 cm^3) + KCl (0.93 g)	10.5
0.05 M $NaHCO_3$ (50 cm^3) + 0.1 M NaOH (23.3 cm^3) + KCl (0.57 g)	10.6
0.05 Na_2HPO_4 (50 cm^3) + 0.1 M NaOH (3.3 cm^3) + KCl (0.24 g)	10.9
0.05 Na_2HPO_4 (50 cm^3) + 0.1 M NaOH (6.3 cm^3) + KCl (0.27 g)	11.2
0.05 M NaOH + KCl (1.49 g)	12.23
0.15 M NaOH + KCl (0.74 g)	12.88
0.25 M NaOH	13.20

For the addition of acidified coupler solutions to aryldiazotates a different method of buffering was developed. The aryldiazotate was first dissolved, or prepared in, a basic solution (A) and the coupler in dilute acid (B). Both (A) and (B) had ionic strength of 0.25 mol dm^{-3}. An example of (A) and (B) is:-

(A): 0.3 M KCl (25 cm^3) + 0.1 M NaOH (50 cm^3)

(B): 0.1 M NaH_2PO_4 (50 cm^3) + 0.1 M HCl (10 cm^3) + KCl (0.67 g)

In (A), the aryldiazotate is quite stable, but on addition of equal volumes of (A) to (B), a buffered solution of pH 12.0 is produced in which the reaction proceeds.

2.2.1 Instruments

The instruments used in the course of this work, unless stated elsewhere, were as follows:

Calculation of correlation coefficients; Texas Instruments SR-56 programmable calculator,

Calculation of gradients and standard deviations by least sqaure analysis; Burroughs B6700 computer,

Ultra-violet and visible spectra; Cary 14, Pye-Unicam SP800 and SP1800 spectrometers,

E.s.r. spectrum; Bruker model no. ER 200 tt.

2.3 Kinetic Procedure

The procedures for each type of reaction are listed below. The reactions were either of first order or were made to adhere to pseudo-first order kinetics with respect to either the arenediazonium salt or the aryldiazotate. Since the initial concentrations of the arenediazonium salts and aryldiazotates are not needed for the determination of rate constants and also because the concentrations are not exactly known due to slight thermal decomposition, samples were not weighed exactly but only approximately in order to obtain a solution which yielded a convenient absorption change on reaction.

2.3.1 (i) The coupling reaction

This group of reactions was carried out by mixing together equal volumes of aqueous arenediazonium salt at ca. pH 5.6 and at relatively low concentration (ca. 0.0001 M) with the coupler at relatively high and accurately known concentration (ca. 0.002 M) and buffered at approximately the desired final pH. This method ensures (a) adherence to a pseudo-first order rate law with respect to the change in arenediazonium ion concentration and (b) maintenance of the arenediazonium salt at a pH which keeps thermal decomposition at a minimum. On mixing the two components, the pH adjusts within the mixing time of the apparatus. When the coupling reaction is very slow and at a fairly high pH, thermal decomposition may be significant and requires compensation as indicated in section 2.4. Solutions of arenediazonium salts were shielded from light with aluminium foil and the coupler solutions were made up in one of three ways.

(a) Most simple hydroxyaromatics were accurately weighed and dissolved in the appropriate buffer, with warming if required, and all were flushed with a stream of nitrogen to prevent aerial oxidation.

(b) The 2,3-dihydroxynaphthalene-metal complexes were insoluble in water except at high pH, and so were first dissolved in methanol (10 cm^3), then made up to 50 cm^3 with the buffer solution. This introduced into the final reaction mixture 10% by volume of methanol. These solutions were used as soon as possible as the coupler slowly decomposed.

(c) Amides, such as acetoacetanilide, hydrolyse slowly in both acid and base,and so were dissolved in a pH 7 buffer solution. U.v. spectra were taken at intervals after solution and no hydrolysis was observed.

The reactions were followed spectroscopically by the appearance of the azo dye product which, possessing highly conjugated systems, absorb light intensely in the visible region.

(ii) The reaction of arenediazonium salts with base

The arenediazonium salts were dissolved in dilute HCl (ca. 0.02 M) made up to an ionic strength of 0.25 mol dm^{-3} with KCl and shielded from the light with foil. The less stable 4-phenylene tetrazonium tetrafluoroborate was dissolved in 0.1 M perchloric acid although, nonetheless, it decomposed fairly quickly. The arenediazonium salts mixed with base buffered at the appropriate pH, except for those at pH > 12, at which solutions of sodium hydroxide (with KCl to give μ = 0.25 mol dm^{-3}) of an appropriate concentration were used, e.g. to obtain pH 13.0, 0.2 M NaOH was required. The conversion of arenediazonium salt to the syn-aryldiazotate was conveniently followed spectroscopically at the λ_{max} of the aryldiazotate. Usually the subsequent isomerisation to the anti-form was followed at the same wavelength, although in some cases comparison of the spectra of the syn- and anti-isomers indicated a more suitable wavelength.

(b) The 2,3-dihydroxynaphthalene-metal complexes were insoluble in water except at high pH, and so were first dissolved in methanol (10 cm^3), then made up to 50 cm^3 with the buffer solution. This introduced into the final reaction mixture 10% by volume of methanol. These solutions were used as soon as possible as the coupler slowly decomposed.

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(iii) The reaction of aryldiazotates with acid

The solutions of aryldiazotate were prepared by mixing together a slightly acid solution of the corresponding arenediazonium salt (ca. 5 cm^3) with aqueous sodium hydroxide (0.05 mol dm^{-3}) to make up the volume to 50 cm^3 and to achieve ca. 0.0005 M aryldiazotate. Arenediazonium salts with strongly electron-withdrawing substituents rapidly gave solutions of stable anti-aryldiazotates, whereas those without such groups give the syn-isomer which slowly isomerises (some also decompose).

These solutions were added to the appropriate buffer solution containing HCl to neutralise the NaOH. The formation of arenediazonium salt was observed spectroscopically by:

(a) the increase in its optical density at λ = ca. 250-300 nm (This method was only satisfactory at low pH);

(b) the appearance of an azo dye produced by the rapid reaction of the arenediazonium salt as it is formed with a suitable coupler usually 2,3-dihydroxynaphthalene-6-sulphonic acid;

(c) the appearance of the decomposition products from the arenediazonium salts which consisted mainly of the corresponding phenol, although this method was found to be rather unsatisfactory;

(d) the disappearance of the aryldiazotate.

In all of the above reactions, (i)-(iii), the ionic strength of all the reactant solutions were made up to 0.25 moles dm^{-3} with KCl,and the final pH of the reaction mixtures measured with a 'Pye' model PW9410 pH meter with a special glass electrode, accurate up to pH 14.0 ± 0.2.

Reactions with $t_{\frac{1}{2}}$ > 20 s were studied conventionally with Pye-Unicam SP800 or SP1800 instruments, or a Cary 14 u.v.-visible spectrophotometer, the technique for each instrument being the same, and is described below. When $t_{\frac{1}{2}}$ < 20 s, recourse was made to the

stopped-flow method, (a) with single wavelength monitoring, (b) by following a 150 nm waveband with the rapid scanning spectrophotometer and (c) a 3-inlet, quenched-flow system for the study of the syn-diazotate intermediate. (These methods are described below).

2.3.2 Technique and data processing for reactions with $t_{\frac{1}{2}} > 20$ s

Equal volumes of the two reactant solutions, previously thermostatted to 25° C, were rapidly mixed in a quartz cuvette and placed in the spectrophotometer. The reaction was followed, depending on its character (see p. 66), either by the appearance of azo dye or the appearance or disappearance of the aryldiazotate absorption peak.

The first or pseudo-first order rate constants (k_1) were found from plots of ln OD_t against time, where the gradient is the rate constant and OD_t is the optical density of the minor reactant, i.e. the arenediazonium salt (ArN_2^+) or the aryldiazotate (ArN_2O^-) at time t. In the case of the coupling reaction where the optical density of the azo dye was followed, referring to Fig. 6 at time t,

$$\left[\text{azo dye}\right]_t = \frac{OD_t}{\varepsilon l}$$

$$\left[\text{azo dye}\right]_\infty = \frac{OD_\infty}{\varepsilon l} = \left[ArN_2^+\right]_o$$

$$\text{therefore } \left[ArN_2^+\right]_t = \left[\text{azo dye}\right]_\infty - \left[\text{azo dye}\right]_t \qquad (70)$$

(N.B. subscripts denote the time)

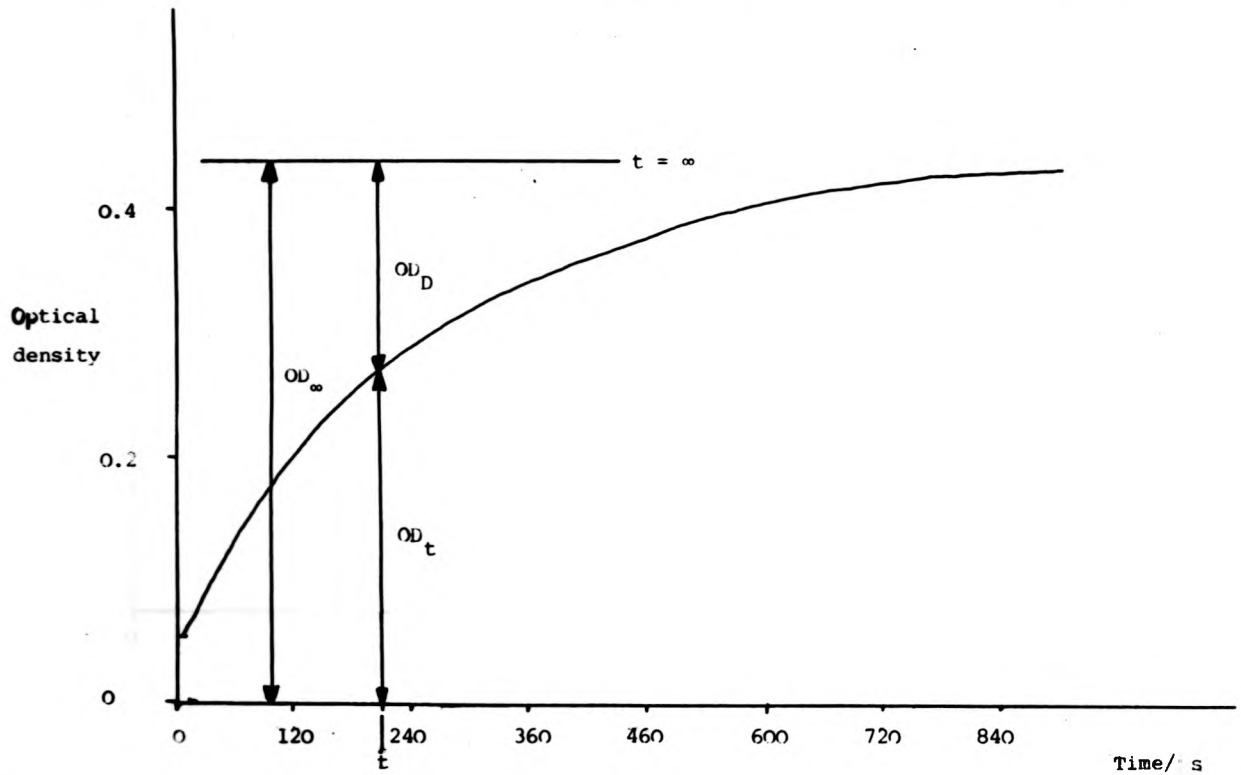
and therefore OD_t can be found from

$$OD_D = OD_\infty - OD_t \qquad (71)$$

where OD_D is related to the optical density of the arenediazonium salt and is conveniently used in the kinetic rate plots.

From the coupling reaction, the pseudo-first order rate

Figure 6 Trace illustrating the increase in optical density with time from the coupling reaction between 4-chlorobenzenediazonium cation and 2,7-dihydroxynaphthalene at pH 5.7



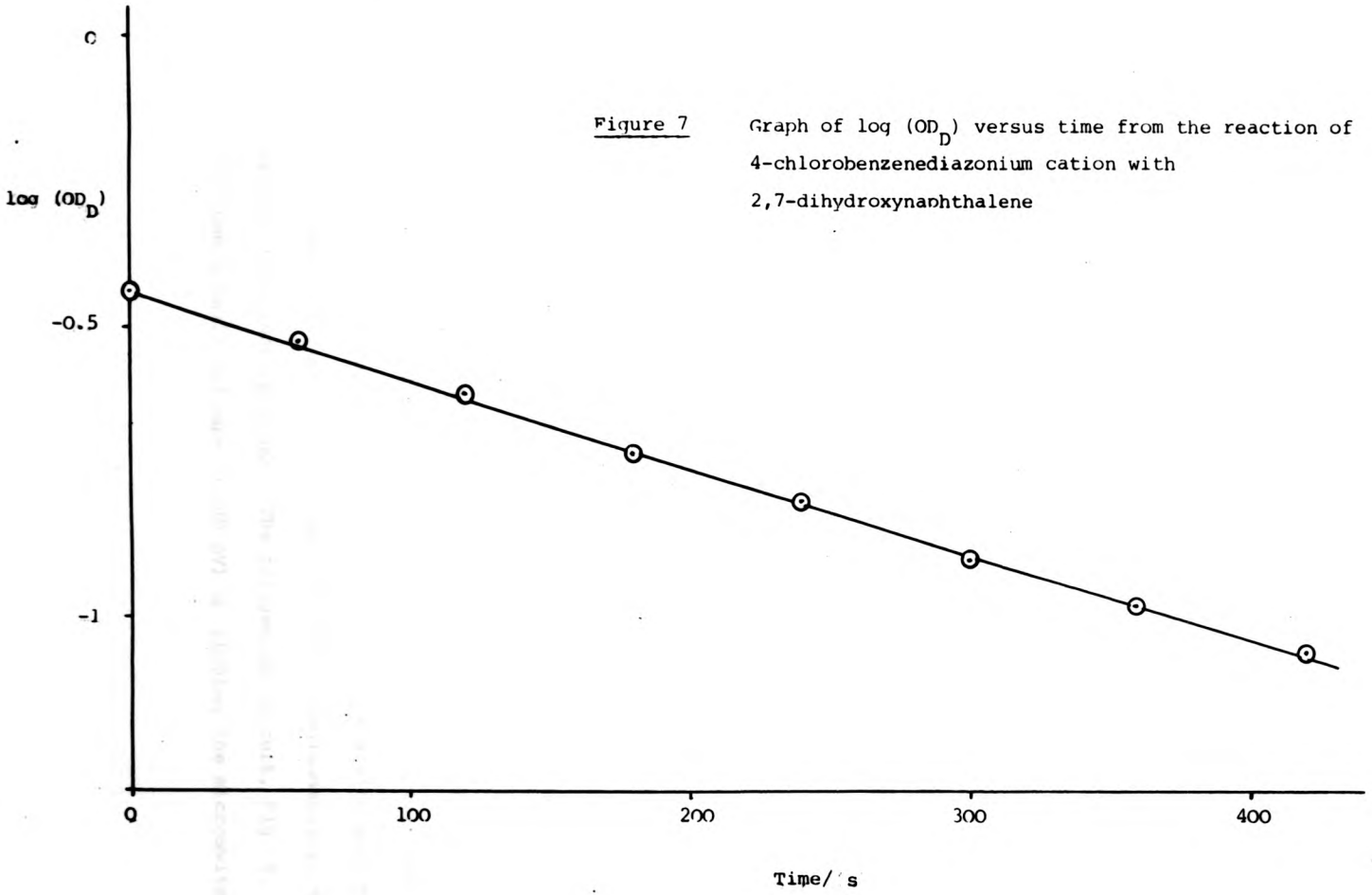


Figure 7 Graph of log (OD_D) versus time from the reaction of 4-chlorobenzenediazonium cation with 2,7-dihydroxynaphthalene

constants, k_1 were converted to the second-order rate constants, k_2, by dividing by the initial coupler concentration, viz.

$$k_2 = \frac{k_1 \times 2}{\text{coupler}} \qquad (72)$$

(The factor of 2 is included because the coupler concentration is halved when the two reactant solutions are mixed). Fig. 6 portrays a typical trace and Fig. 7 the corresponding analysis from the reaction of 2,7-dihydroxynaphthalene with 4-chlorobenzenediazonium tetrafluoroborate at pH 4.57.

2.3.3 Technique and data processing for reactions with $t_{\frac{1}{2}} < 20$ s

The stopped-flow apparatus used with (a) single wavelength monitoring and (b) the rapid scanning spectrometer are almost identical to that described by Gibson et al.[160] We have used the single wavelength equipment modified by Matts[163] and featuring a transient recorder, and also the version improved by Moore;[175a] both are described below.

(i) The stopped-flow apparatus

Description.- The apparatus, Fig. 8, consists of two drive syringes (D) into which the two reactant solutions are loaded. These are driven by a hydraulic ram (R), through a special mixing device which consists of eight jets, positioned at right angles to each other and are directed tangentially into a slightly wider tube (2 mm diameter) which is connected to a quartz cell and finally to the stop-syringe which triggers, via a microswitch (MS) a Tektronix storage oscilloscope (CRO) and, simultaneously, a Datalab transient recorder. The triggering circuit, Fig. 9, produces a small voltage (0.188 mV) on closing the microswitch (MS).

Fig.8 The stopped-flow apparatus

KEY:-

A = reservoir syringes

D = drive syringes

R = hydraulic ram

1-5 = values

S = stop syringe

L = light source

M = monochromator

C = quartz windows

PM = photomultiplier tube

HT = high voltage power supply

MS = microswitch

T = trigger circuit

W = waste

CRO = storage oscilloscope

TR = transient recorder

MA = microammeter

CR = chart recorder

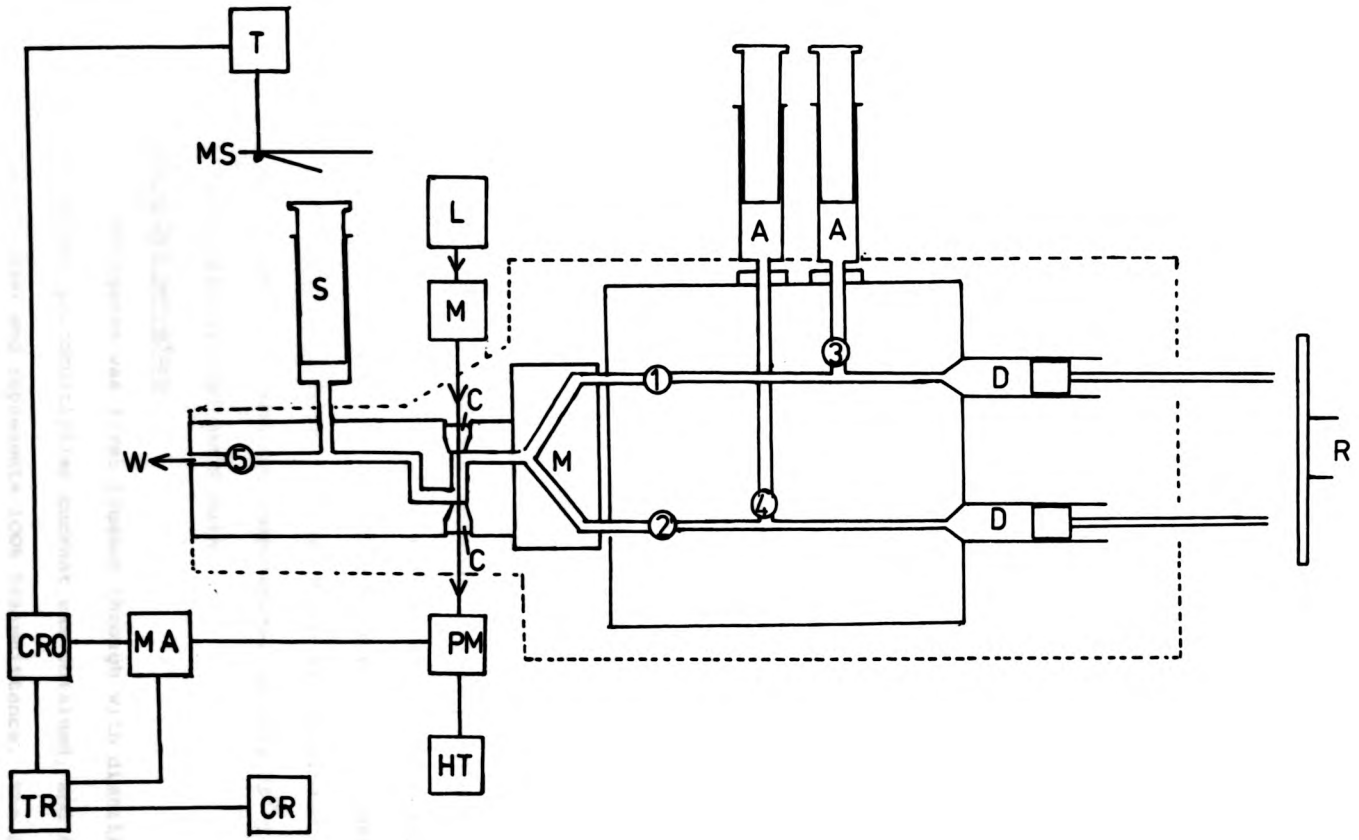
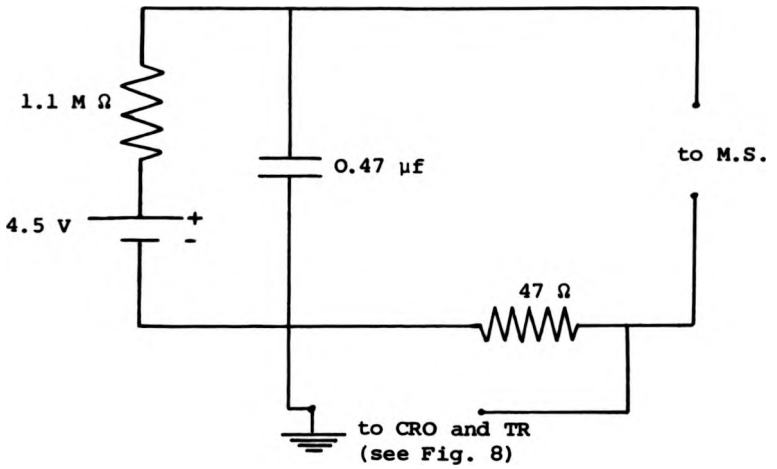


Fig. 8 The stopped-flow apparatus

Fig. 9 Circuit diagram of the triggering circuit



The reaction is followed photometrically through the quartz cell (C) with a monochromated light source (L and M) and an EMI type 9781R photomultiplier tube (PM) (with all dynodes connected with 100 K resistors) as detector. The photomultiplier current, followed with a microammeter, is amplified and displayed on the oscilloscope screen (CRO) and at the same time recorded by the transient recorder (TR). The oscilloscope display can be photographed with a polaroid camera or, more usually, the transmittance-time curve output from the transient recorder (TR) is plotted with a servoscribe chart recorder (CR). With relatively slow reactions ($t_{\frac{1}{2}} \sim$ 20 s), the amplified photomultiplier current was passed directly to the chart recorder. In Fig. 8 the area enclosed by the dashed line is kept at a constant temperature, usually 25° C $\pm 0.2^{\circ}$ C, with a thermostatted water bath.

Operating procedure

The system was first flushed through with distilled water until a constant photomultiplier current was obtained, and this voltage was recorded and represents 100% transmittance. The corresponding

Figure 10 Typical trace obtained with the stopped-flow apparatus from the reaction of syn-4-chlorobenzenediazotate and 2-naphthol at pH 12.88

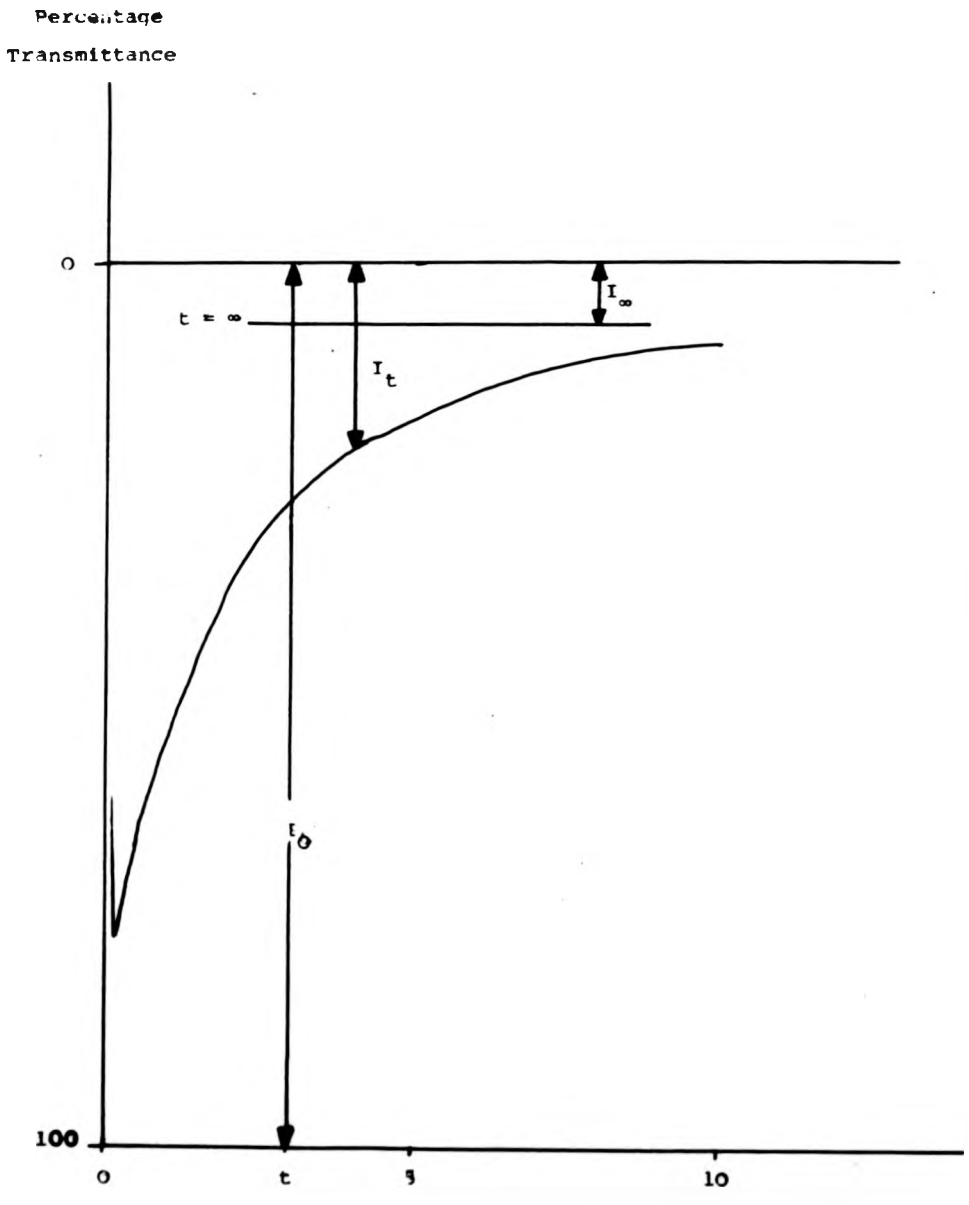


Figure 11 . Computer plot of optical density against time for the reaction of syn-4-chlorobenzenediazotate with 2-naphthol

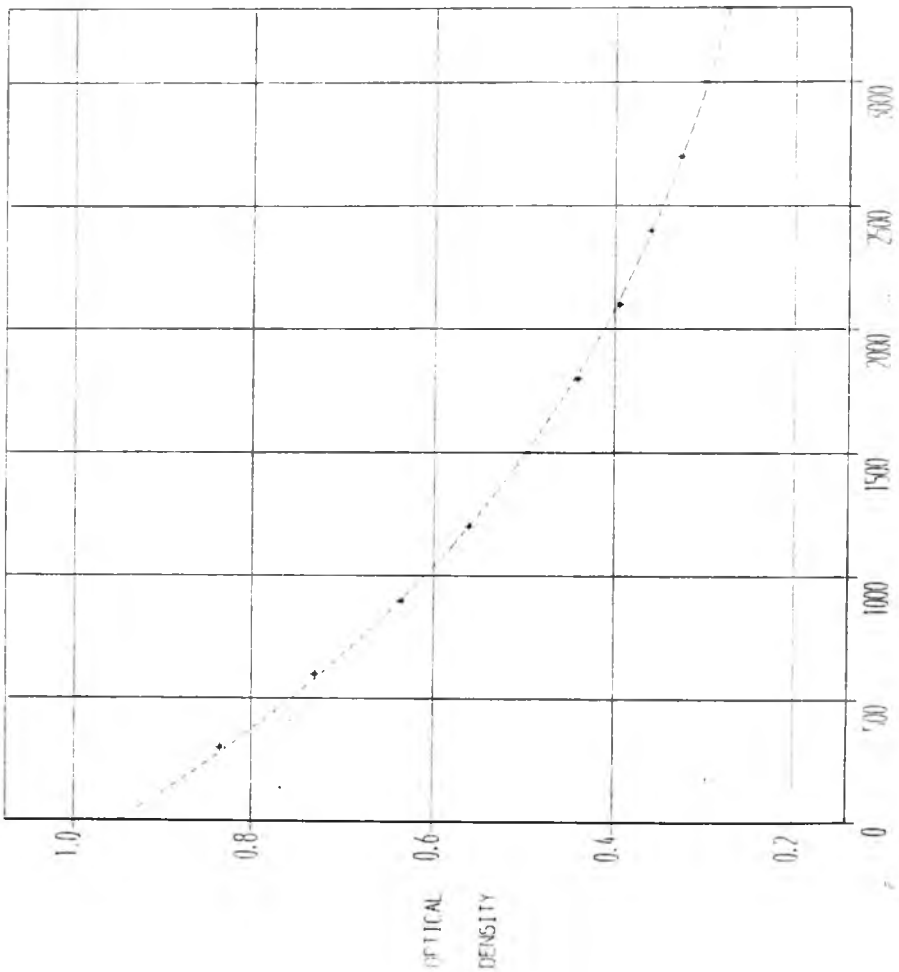


Figure 11 . Computer plot of optical density against time for the reaction of syn-4-chlorobenzenediazotate with 2-naphthol

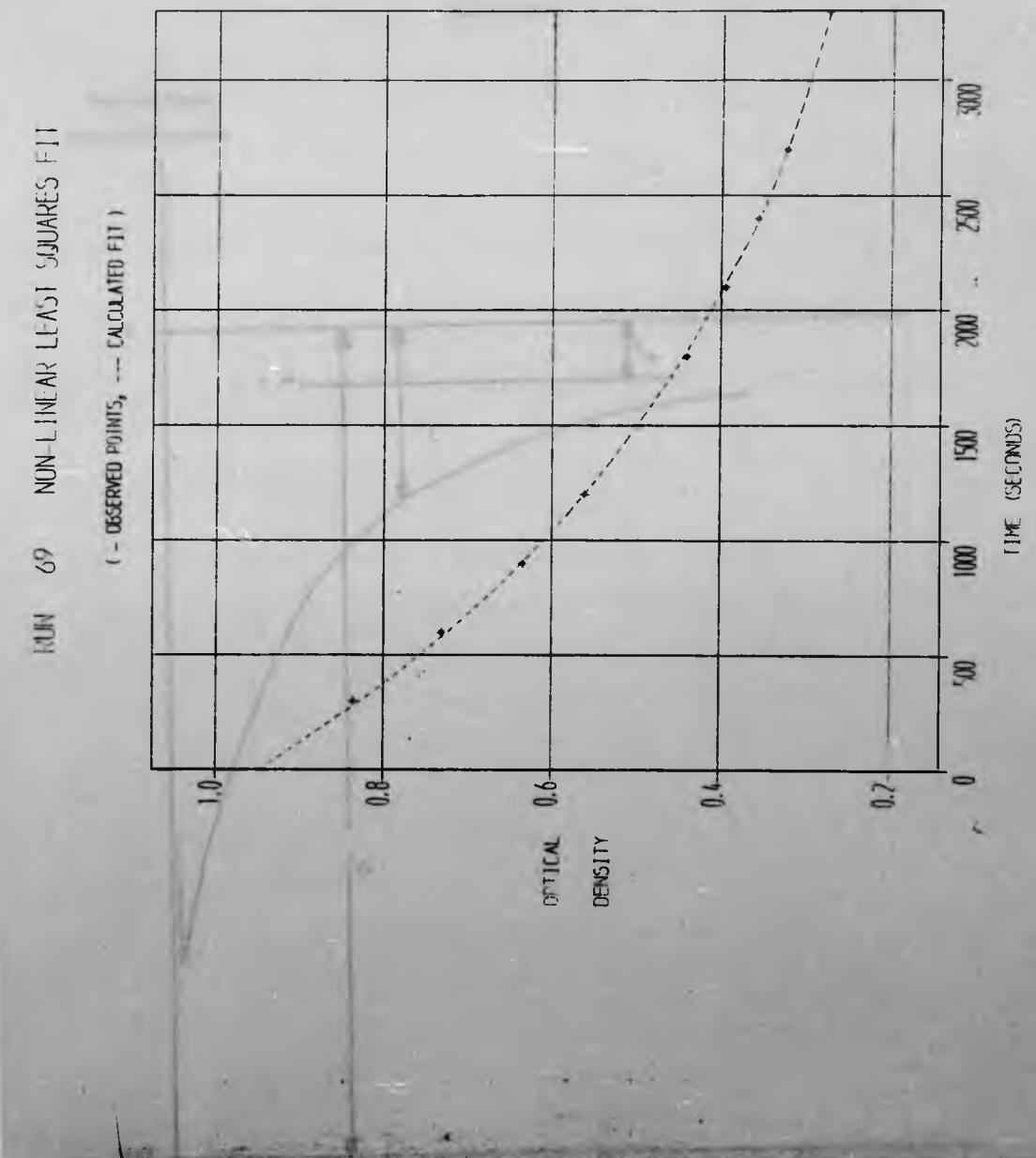


Figure 12. Computer plot of $\ln(OD_t - OD_\infty)$ against time for the reaction of syn-4-chlorobenzenediazotate with 2-naphthol

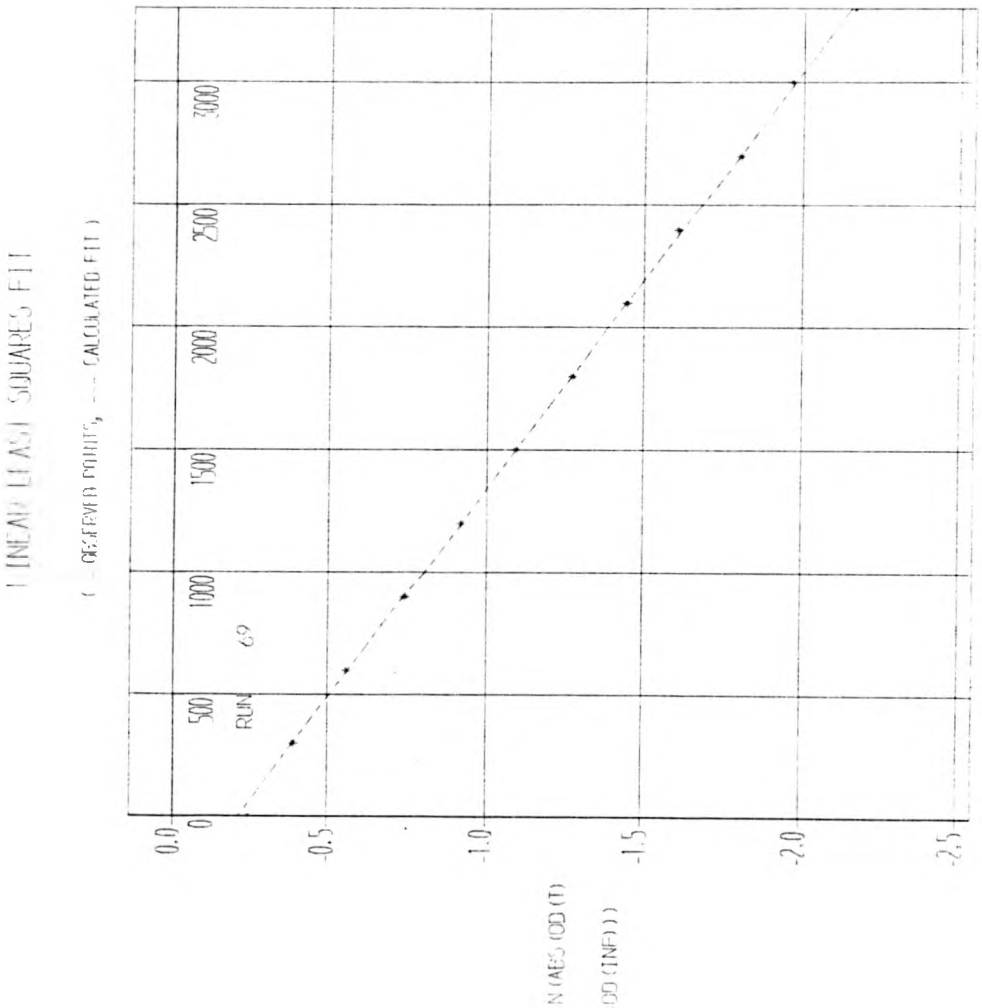
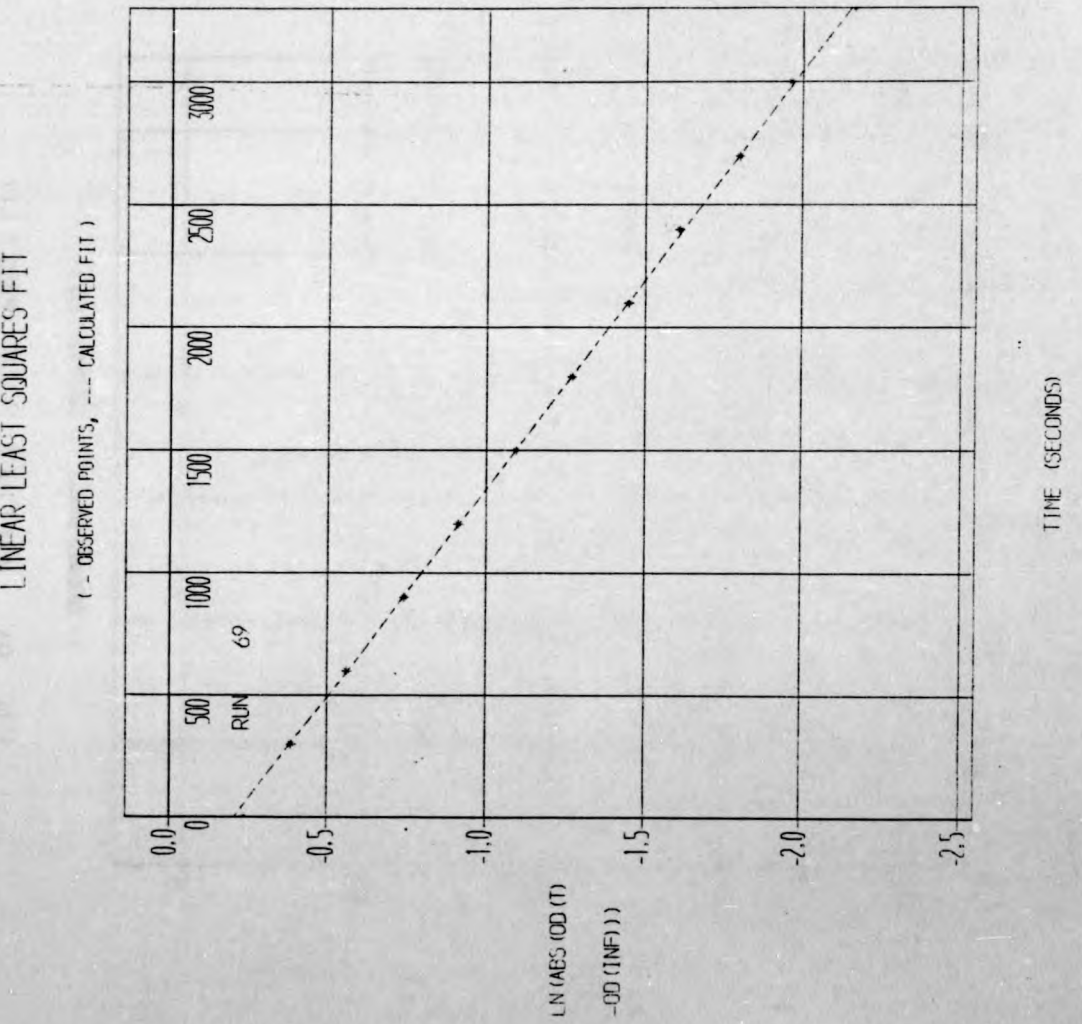


Figure 12. Computer plot of $\ln(OD_t - OD_\infty)$ against time for the reaction of syn-4-chlorobenzenediazotate with 2-naphthol



0% transmittance value was found by blocking the light source. The drive syringes were then filled with reactant solutions with valves 3 and 4 open and valves 1 and 2 closed. Ca. 1.0 cm^3 of each was run through the apparatus with valves 1, 2 and 5 open and 3 and 4 closed. The drive syringes (S) were then refilled and allowed to reach the water bath temperature. A number of runs, with valves 3, 4 and 5 closed and 1 and 2 open, were made to ensure that the curves displayed on the oscilloscope (CRO) were consistent, and then the last of these was finally recorded with the transient recorder (TR) and plotted on to the chart recorder. On completion of the reaction, the infinity value of the photocurrent was measured. A typical example of the results, consisting of the 100%, 0%, infinite transmittance values and the rate plot are depicted in Fig. 10 for the reaction between syn-4-chlorobenzenediazotate and 2-naphthol at pH 12.88.

Calculation of rate constants

The first or pseudo-first order rate constants were computed with the aid of a Burroughs B6700 computer, using a computer program based on one due to Moore.[176,177] With this program, if the infinity photocurrent is unknown for example with the first of a two-stage process or when the product is unstable, the computer will calculate this value from the available data points by non-linear least squares analysis. The subsequent stages of the program are as follows:-

(a) conversion of transmittance readings to optical density (OD) by the equation

$$OD = \log(I_o/I_t) \qquad (73)$$

(b) the gradient, (k_1), of a plot of time versus ln (OD_∞-OD) is calculated by a linear least squares analysis, the gradient being the first order rate constant, k_1

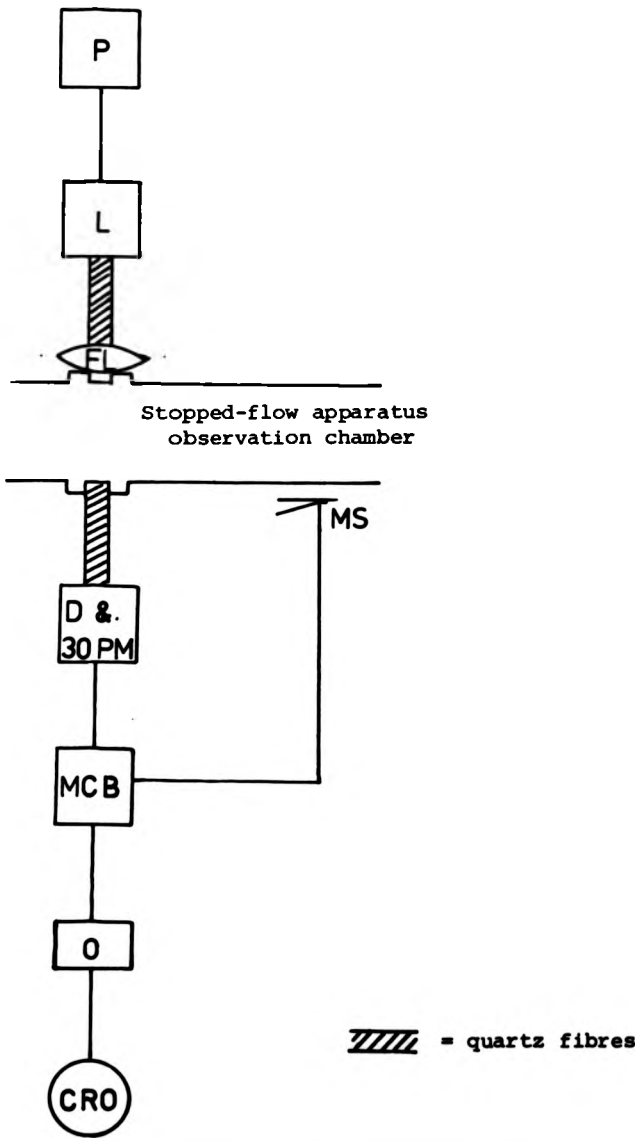
Figure 13

The rapid-scanning spectrometer

KEY:-

P	=	Power supply
L	=	Xenon arc lamp
FL	=	Focussing lens
D	=	Diffraction grating
PM	=	Photomultiplier
MS	=	Microswitch
MCB	=	Multiplexing control box
O	=	Offset
CRO	=	Oscilloscope

Fig. 13 The rapid-scanning spectrometer



N.B. $OD_\infty = \log (I_o/I_\infty)$ (74)

where I_∞, I_o and I_t are as in Fig. 10.

c) The computer finally plots graphs of (i) optical density (OD) against time and (ii) of ln $(OD_\infty - OD)$ against time, examples of which are given in Figs. 11 and 12, for the reaction of syn-4-chlorobenzenediazotate and 2-hydroxynaphthalene at pH 9.04.

The second order rate constant for the overall reaction

$$ArN_2^+ + 2OH^- \xrightarrow{k_2} \underline{syn} - ArN_2O^- + H_2O \qquad (75)$$

may be calculated from the pseudo-first order rate constant k_1 by

$$k_2 = \frac{k_1}{[OH^-]} \qquad (76)$$

As described in section 1.2.6 (reaction 16), 2-4-dinitrobenzenediazonium salts and other arenediazonium salts[178] with strongly electron-withdrawing groups hydrolyse to diazophenols and therefore a correction must be made in order to calculate rate constants. Sterba[178] noted that as the pH was increased (above pH_m), the effect of hydrolysis became relatively smaller compared to k_2, and he also found that the diazotates so formed do not hydrolyse.

If the rate of hydrolysis is k_h, then the true pseudo-first order rate constant k_1 may be calculated from the observed (apparent) rate constant k_A by

$$k_A = k_h + k_1 \qquad (77)$$

Second order rate constants, k_2, were simply calculated from pseudo-first order rate constants k_1 by eqn. (76) as described above.

(ii) <u>The rapid scanning spectrophotometer</u>

<u>Description</u>.- The Applied Photophysics (London) 'Multiplex Spectrometer', model 610 (Fig. 13), produces repetitive, fast

time-resolved spectra. Light from a 150 W xenon arc lamp (L) passes through the observation chamber of a conventional stopped-flow apparatus and then travels along a quartz fibre optic to a diffraction grating (D) which gives a spectrum in the plane of a row of quartz optical fibres which are split up into thirty five-nm bunches. Each bunch of fibres is connected to a 1P28 photomultiplier tube (PM) which, in turn, is connected to the multiplexing control box (MCB). The multiplexing control box amplifies each signal and then corrects them for the difference in response from the photomultipliers. It outputs the 30 signals as a complete spectrum in 80 μs as often as required, from 0.5 ms to 5 s, on to a Tektronix 5115 storage oscilloscope (CRO) which is then photographed with a polaroid camera. The function of the offset (O) is to enable the sensitivity of the oscilloscope to be changed without altering the position of the 100% transmittance level on the screen.

The stopped-flow apparatus incorporated in this device is basically the same as the one described previously (section 2.3.3(i)) but with some modifications.[175a]

(a) The mechanical hydraulic ram is replaced by one operated by air pressure.

(b) Each drive syringe, reservoir and thermostatted tube which connects to the mixing blockhousing is made from one piece of glass.

(c) The thermostatting fluid (pumped around the apparatus by a Churchill pump) passes along the whole length of the apparatus through tubes which are as close as possible to those containing the reactants and reaction mixture, to ensure better temperature control. The fluid passes from the PTFE mixing blockhousing into each thermostatting tube by six small holes, which are separated from the reactant tube by rubber 'O'-rings (see Fig. 14).

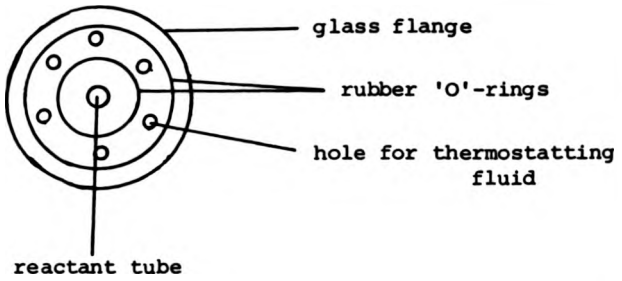


Fig. 14 Diagram illustrating glass flange which connects to the PTFE housing for the mixing block

Procedure

(a) To protect the circuitry from the high voltage starting pulse, the arc lamp is struck before the multiplexing control unit is plugged in and switched on.

(b) The stopped-flow apparatus is flushed with water.

(c) The 30 gain controls turned to their maxima and the 3 high voltage supplies to the photomultipliers gradually increased (one at a time), to limit the largest individual photomultiplier voltage to 9 volts in each of the three groups of 10 signals.

(d) The gain controls are adjusted to synchronise all of the photomultiplier signals to the same voltage, corresponding to 100% transmittance. Blocking the light source enables the zero transmittance voltage to be measured, and the two voltages, corresponding to 100% and 0% transmittance, are recorded.

(e) The reactant solutions are placed in the reservoirs and the stopped-flow apparatus flushed through with ca. 5 cm^3 of each.

(f) A number of kinetic runs are performed to ensure good reproducibility and, with various time intervals beween spectra, to ensure that all stages of the overall reaction are observed. When the reaction is complete, the final spectrum is recorded.

The rate constants are calculated as with the single wavelength monitoring device.

(iii) Three-inlet quenched-flow apparatus

Sterba et al.[130] have studied the N-O bond splitting of aryldiazohydroxides in aqueous solution to yield arenediazonium ions; however, they omitted all syn-aryldiazotates with strongly electron-withdrawing 2- and 4-substituents as these isomerise rapidly to give the corresponding anti-form. In order to extend investigation of this reaction to such compounds, it is necessary to reduce the pH of the syn-aryldiazotate solution as soon as possible after it is formed. To achieve this, we have designed and built an apparatus on the 'quenched-flow' principle, but incorporating spectrophotometric observation of the 'quenching' process.[160]

The apparatus (Figs. 15 and 16) consists of three drive syringes (1-3), two of which (1 and 2) contain (1) the arenediazonium salt solution and (2) aqueous NaOH which mix, after thermostatting, at mixer 1 (M1) to give (by the time the mixture reaches mixer 2 (M2)) the corresponding syn-aryldiazotate. At mixer 2 (M2), buffer from syringe (3) is added to the newly-formed syn-compound to give immediately a certain amount of aryldiazohydroxide which, in turn, rapidly yields the arenediazonium ion. The appearance of the latter is monitored spectrophotometrically through the quartz windows (Q) and the monochromated light (M and L) detected with an EMI type 9781R photomultiplier tube (PM) with all dynodes connected with 75 K resistors. The amplified signal is displayed on a Tektronix type 564 storage oscilloscope (CRO) and simultaneously recorded with a Datalab transient recorder (TR). The transmittance-time curves are then plotted with a Servoscribe chart recorder (CR). The three drive syringes (1-3) are filled from three reservoirs with taps (1)-(3) open and (4)-(6) closed, and

Figures 15 and 16 The quenched stopped-flow apparatus

KEY:-

RES	Reservoir (X3)
DS	Drive syringe (X3)
MS	Microswitch
R	Rack
P	Pinion
M	Motor
T1	Thermostating fluid inlet
TO	Thermostating fluid outlet
M1	First mixer
M2	Second mixer
Q	Quartz windows (X2)
W	Waste outlet
BN	Brass nut (X3)
PS	Motor power supply
L	Lamp
MO	Monochromator
FL	Focusing lens
PM	Photomultiplier tube
MA	Milliammeter
CB	Control box
CRO	Oscilloscope
DR	Data recorder
CR	Chart recorder
1 - 6	Taps
▨	P.T.F.E. blocks

Figure 15 Side view of quenched stopped-flow apparatus

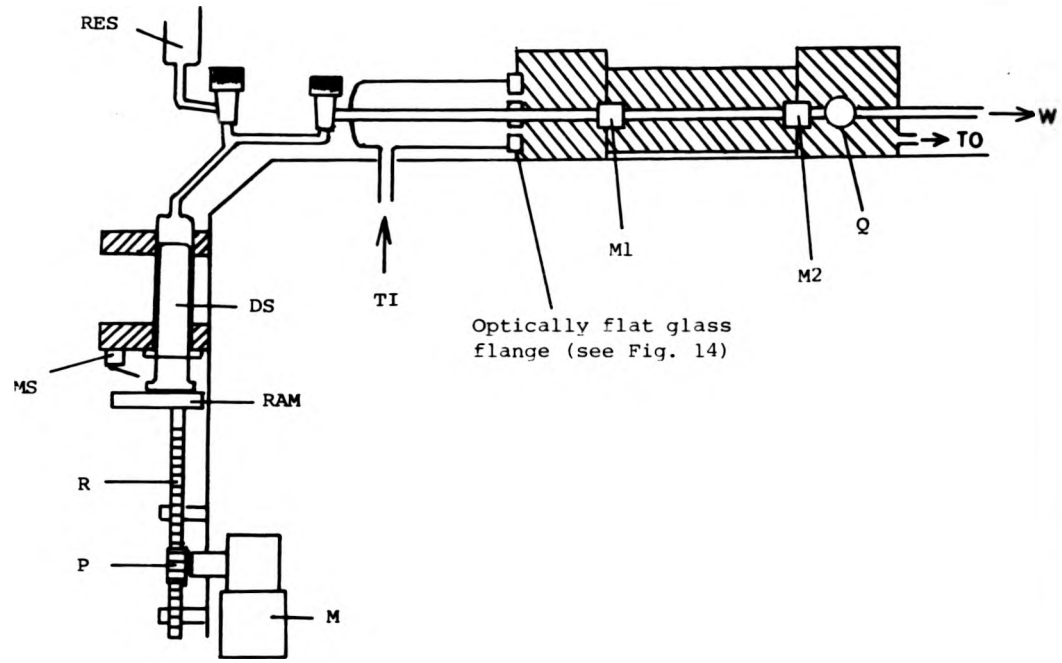
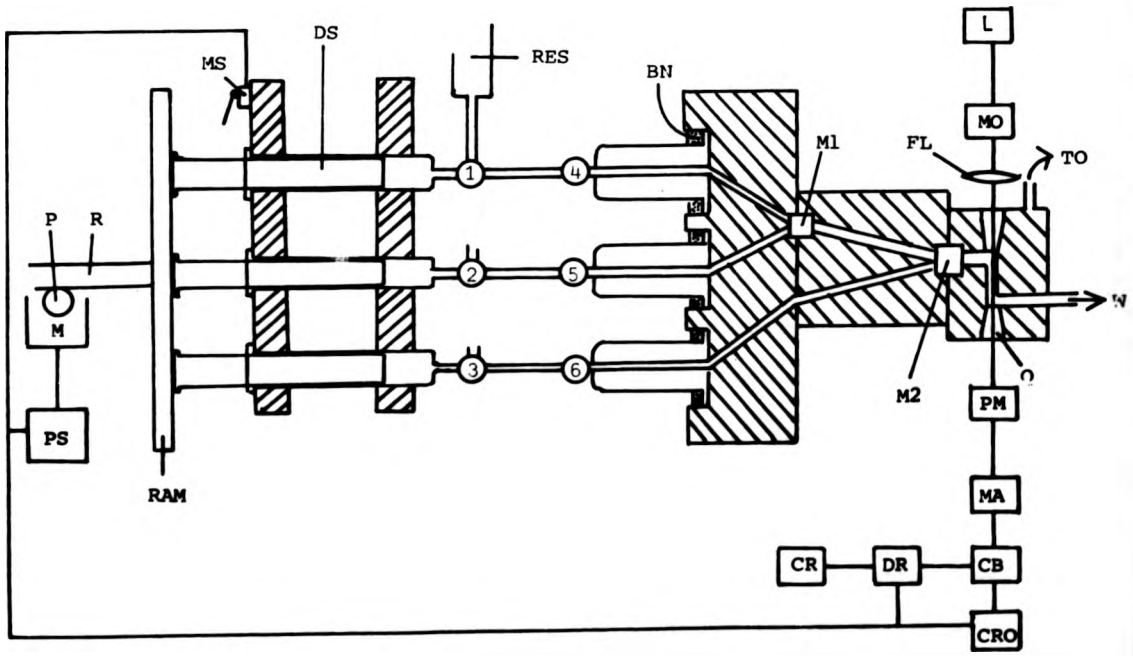


Figure 16 Top view of quenched stopped-flow apparatus



then with (1)-(3) closed and (4)-(6) open, they are driven by a variable speed DC motor (powered by a stabilized power supply) connected *via* a rack and pinion drive to the ram (R). Once the system has been flushed through, the ram is stopped and simultaneously the motor is switched off and the oscilloscope and transient recorder triggered to record the reaction profile. The power supply to the electric motor incorporates a reverse-polarity switch so that the ram (R) can be conveniently reversed prior to refilling the syringes.

The apparatus is thermostatted by pumping water through the apparatus with a Churchill pump, first through the jackets surrounding the three reactant tubes and then through the PTFE blocks along tubes which lie within 1 cm of the reactant tubes. The glass sections of this apparatus are similar to those used in the stopped-flow apparatus with the rapid-scanning spectrometric monitoring, except that the drive syringes are at right angles to the direction of flow through the rest of the apparatus.

The drive syringes are driven at a speed such that, during the time taken to pass between the two mixers (t), a maximum yield of the *syn*-aryldiazotate is obtained, but with as little of the *anti*-form as possible. The times required to achieve such conditions were found from data obtained with the rapid-scanning spectrometer. The speed control was calibrated as follows:- the reaction of 3-chlorobenzenediazonium cations with sodium 2,3-dihydroxynaphthalene-6-sulphonate at *ca.* pH 6.5 was monitored,firstly using drive syringes (2) and (3) so as to commence the reaction at the exit from mixer 2 (M2), and, secondly, using syringes (1) and (2) to begin coupling at the exit from mixer 1 (M1). In the latter case, the reacting solution has to travel between the two mixing blocks before observation of the azo dye formation commences, and so by

comparison of the transmittance at the beginning of the two traces so obtained, one can evaluate the transit time (t). By recording the transmittance-time curves obtained with different motor speed control settings, their corresponding times (t) can be measured similarly. A range of times (t) between 0.3 s and 2 s were found to be feasible. The reaction between Fe(II) and SCN^- was used to ascertain the accuracy of the rate constants obtained with the apparatus and the results were found to be within 10% of the literature values.[179] The main inaccuracy is probably due to the relatively long mixing time of nearly 0.2 s. This problem could probably be diminished in the future by the incorporation of a 'stop-syringe' as in the conventional stopped-flow apparatus (Section 2.3.3i).

For the determination of the rate constants of N-O bond splitting of substituted syn-aryldiazohydroxides (k_{-1}) the solutions used in the three syringes were typically as follows:-

(1) 0.005 M HCl + 10^{-4} M ArN_2^+ made up to an ionic strength (μ) of 0.25 mol dm^{-3} with KCl.

(2) 0.05 - 0.1 M NaOH made up to μ = 0.25 mol dm^{-3} with KCl (NaOH concentration varied to give a range of pH).

(3) 0.2 M NaH_2PO_4 + 0.05 M KCl.

The calculation of k_{-1} from the apparent first-order rate constants is discussed later in section .

2.3.4 Conversion of k_2 to the absolute rate constant

The second order rate constants (k_2) found from coupling reactions is defined by (19) (see p. 17).

$$\frac{d[Az]}{dt} = k_2 [D][C] \qquad (19)$$

However, where [C] is a hydroxy aromatic coupler, k_2 is pH-dependent because of the equilibrium:

$$ArOH \rightleftharpoons ArO^- + H^+ \qquad (78)$$

It is convenient to convert k_2 to an absolute rate constant (k) which is independent of pH and equivalent to coupling with 100% of the reactive species, i.e. the phenolate or naphtholate anion. The absolute rate constant (k) has been defined by Zollinger:[64,70]

$$\frac{d[Az]}{dt} = k\left[Ar—N_2^+\right]\left[ArO^-\right] \qquad (32)$$

where $\frac{d[Az]}{dt}$ is the rate of azo dye formation

$[D]$ and $\left[Ar—N_2^+\right]$ are the arenediazonium salt concentration

$[C]$ is the coupler concentration

$\left[ArO^-\right]$ is the concentration of the ionised form of the coupler

The proportion of coupler anion may be calculated from (78) with

$$K_A = \frac{\left[ArO^-\right]\left[H^+\right]}{[ArOH]} \qquad (79)$$

where K_A is the acid dissociation constant.

Equating (19) and (32) and also substituting for $\left[ArO^-\right]$ from (79) yields

$$\frac{k\left[Ar—N_2^+\right][ArOH]K_A}{\left[H^+\right]} = k_2[D][C]$$

but $[D] = \left[Ar—N_2^+\right]$ and $[C] = [ArOH]$

therefore $$k = \frac{k_2\left[H^+\right]}{K_A}$$

and, taking logarithms,

$$\log k = \log k_2 + pK_A - pH \qquad (80)$$

This equation is correct up to $pH = pK_A$ value of the coupler, but above this $k_2 = k$ as $\left[ArO^-\right]$ becomes equal to $[ArOH]$. However at high pH, arenediazonium salts, especially those with electron-withdrawing ring-substituents, react with base to give aryldiazotates (see Section 1.9). Thus, at $pH \geq pH_m$ a further correction is needed to obtain k if the rate of formation of diazotate is equivalent or greater than the rate of azo dye formation.

From Section 1.9

$$K = K_{A1}K_{A2} = \frac{\left[ArN_2O^-\right]\left[H^+\right]^2}{\left[ArN_2^+\right]} \quad (53)$$

Also $$\left[ArN_2^+\right] + \left[Ar{-}N_2{-}O^-\right] = \left[ArN_2^+\right]_S \quad (81)$$

where $\left[ArN_2^+\right]_S$ is the stoichiometric concentration of arenediazonium ions while $\left[ArN_2^+\right]$ refers to the true concentration of this species.

Equating (53) and (81)

$$ArN_2^+ \left\{1 + \frac{K_{A1}K_{A2}}{\left[H^+\right]^2}\right\} = \left[ArN_2^+\right]_S \quad (82)$$

Also $$\frac{d\left[Az\right]}{dt} = k_2\left[ArN_2^+\right]_S\left[ArO^-\right] = k\left[ArN_2^+\right]\left[ArO^-\right] \quad (83)$$

$$\text{therefore } k = k_2\left[1 + \frac{K_{A_1}K_{A_2}}{[H^+]^2}\right]$$

$$= k_2\left[\frac{[H^+]^2 + K_{A1}K_{A2}}{[H^+]^2}\right] \quad (84)$$

Taking logarithms,

$$\log k = \log k_2 + \log\{\left[H^+\right]^2 + K_{A1}K_{A2}\} - \log\left[H^+\right]^2 \quad (85)$$

At high pH, $\left[H^+\right]$ is very small and so $\left[H^+\right]^2$ is negligible,

hence $$\log k = \log k_2 + 2pH + \log K_{A1}K_{A2}$$

$$= \log k_2 + 2\,pH - \left[\frac{pK_1 + pK_2}{2}\right] \quad (86)$$

Values for $(pK_1 + pK_2)/2$ have been found for a number of arenediazonium cations (see Section 1.9).

In this general area of work there are further complications:-

(i) If the coupler has a high pK_A value, e.g. 2-naphthol with pK_A = 9.91[65] and the arenediazonium salt a low pH_m value, e.g. 4-nitrobenzenediazonium salts with pH_m = 9.44, then in the pH range 8.5 - 10.5 neither reactant is present at 100%, which further complicates the calculation. For this reason, it was found to be convenient to measure rate constants well below both the pH corresponding to the pK_A value of the coupler and below the pH_m value of the arenediazonium cation.

(ii) Some of the couplers studied in this project had two hydroxyl

groups which inevitably have different pK_A values, usually separated by at least two units of pH, and hence only at low pH can the coupler be regarded as a singly ionised specie. At pH values above pK_{A1}, but below pK_{A2}, the first hydroxyl group is regarded as being 100% ionised and equation (80) could be used for calculation of the absolute rate constant for 100% of the di-ionised form.

2.3.5 pK_A values

Most of the pK_A values used in this work were taken from the literature, but the others were measured by two methods:-

(i) With compounds such as 1,8-dihydroxynaphthalene, the proton of the hydroxyl group in the mono-ionised species interacts *via* an extraordinarily strong hydrogen bond to the neighbouring ionised oxygen atom, thereby greatly lowering the tendency of the second hydroxyl group to ionise,[96] *i.e.* see p. 26.

As a result, there is an anomalously large difference between pK_{A1} and pK_{A2} and to determine these constants its aqueous solution (*ca.* 0.01 M) was titrated against sodium hydroxide solution (*ca.* 0.2 M) and the pH followed with a PYE model PW 9410 pH meter with a glass electrode. pK_{A1} was found from a plot of pH against the volume of added NaOH (V) and then more accurately from a plot of $\Delta pH/\Delta V$ against V. pK_{A2} was too large to be measured.

(ii) The pK_A values of dihydroxynaphthalene compounds which are incapable of hydrogen bonding such as in (XIV), and therefore with a smaller difference between pK_{A1} and pK_{A2} were measured by a more sensitive method based on that due to Sakaguchi *et al.*[171] A solution of the coupler (50 cm at *ca.* 0.0001 M) was stirred in the dark with a nitrogen stream. Its pH and u.v. spectrum were recorded and then 0.1-0.2 cm^3 portions of aqueous NaOH (0.05 M) were added slowly and its u.v. spectrum recorded in full after each

addition. Finally, when the pH had exceeded ca. 12.5 a small quantity (ca. 0.5 cm^3) of concentrated NaOH-solution was added and the spectrum of the fully di-ionised form recorded. The 'pure' spectrum of the singly ionised species was selected from the family of spectra as that at the change in the spectra (with pH) which went through either a maximum or a minimum. Suitable wavelengths were chosen at which (a) the optical density change of the second ionisation stage was as small as possible and (b) at which the optical density change of the first stage was minimal. From (a), if A_1 is the unionised form, A_2 is the absorbance of the 'fully' singly ionised form and A the absorbance of the partially ionised form, if a graph of pH against $\log \frac{(A_2-A)}{(A-A_1)}$ is plotted, from the equation

$$pH = pK_{A1} - \log \frac{(A_2-A)}{(A-A_1)} \qquad (87)$$

then pK_{A1} = pH when $\log \frac{(A_2-A)}{A-A_1)} = 0$, i.e. when $A_2-A = A-A_1$. pK_{A2} is calculated by the same method, utilizing (b), i.e. if A_3 is the absorbance of the fully di-ionized form, then from a plot of pH against $\log \frac{(A_3-A)}{(A-A_2)}$, at $\log \frac{(A_3-A)}{(A-A_2)} = 0$, pH = pK_{A2}.

The pK_A values for 1,5-dihydroxynaphthalene could not be found as pK_{A1} was too close to pK_{A2} and the spectrum of the singly ionised form was not observable.

Table 8 pK_A values

Coupler	pK_A values	Source
2,3-dihydroxynaphthalene-6-sulphonic acid	pK_{A1} = 8.24	ref. 93
	pK_{A2} = 13.13	
2,3-dihydroxynaphthalene	pK_{A1} = 8.95	ref. 94
	pK_{A2} > 13	
2-naphthol-6-sulphonic acid	8.94	ref. 68
2-naphthol-7-sulphonic acid	8.8	ref. 99
2-naphthol	9.91	ref. 63
1,8-dihydroxynaphthalene	pK_{A1} = 6.35	this work
2,7-dihydroxynapthalene-3,6-disulphonic acid	pK_{A1} = 8.92	this work
	pK_{A2} = 11.10	this work

(continued on next page)

Table 8 (continued)

Coupler	pK_A values	Source
1,8-dihydroxynaphthalene-3,6-disulphonic acid	pK_{A1} = 5.53	ref. 93
	pK_{A2} > 12.75	ref. 93
	pK_{A1} = 5.44	ref. 171
2,7-dihydroxynaphthalene	pK_{A1} = 8.70	this work
	pK_{A2} = 11.26	this work

2.4 Determination of the yield of azo dye from the coupling reaction

Zollinger,[98] in his study of the kinetics of coupling of arenediazonium salts to certain couplers, measured the yield of azo dye produced by a method similar to our own (described below) in order to obtain more accurate rate constants. For example, he used a figure for the yield of 89.2% for the coupling reaction between 4-chlorobenzenedizonium salts with 2-naphthol-6-sulphonic acid to calculate a stoichiometric rate constant of 3 460 $dm^3mol^{-1}s^{-1}$. Using the same percentage yield, we have obtained a value of 3 350 $dm^3mol^{-1}s^{-1}$.

The apparatus[178] for determination of azo dyes by reduction by Ti^{III} (equation 88) is shown in Fig.17 and consists of a

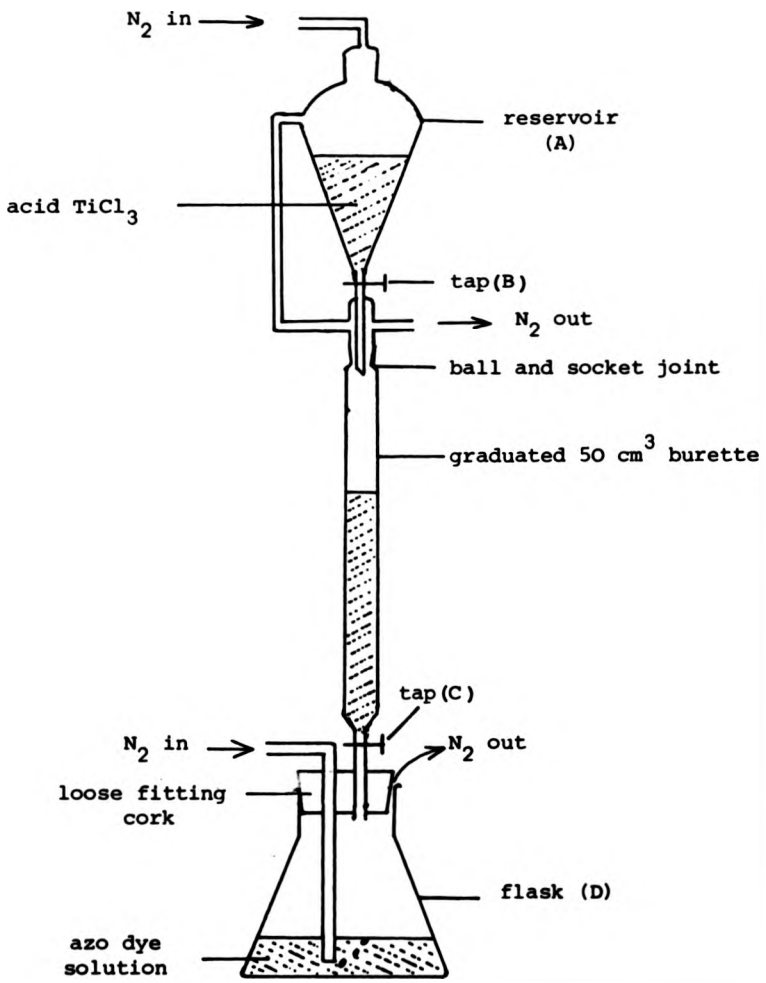
$$Ti^{III}Cl_3 + RN_2R' + 4HCl \longrightarrow RNH_2 + R'NH_2 + 4TiCl_4 \qquad (88)$$

graduated burette and a reservoir in which the contents are continuously flushed with a stream of nitrogen to prevent oxidation of the Ti^{III} to Ti^{IV}.

Method: The stock solution of $TiCl_3$ is prepared by the addition of 15% $TiCl_3$ solution (50 cm^3) to previously boiled and N_2-flushed, cold, dilute 2 M HCl (100 cm^3) and then stored in A. The entire apparatus is flushed continuously with nitrogen. The burette is filled with $TiCl_3$ solution and the sample of azo dye to be analysed (in dilute HCl) placed in the flask, D, and flushed with nitrogen for 15 minutes. An excess of $TiCl_3$ solution is added (of accurately known volume) and, after removal from the automatic burette, the

Figure 17

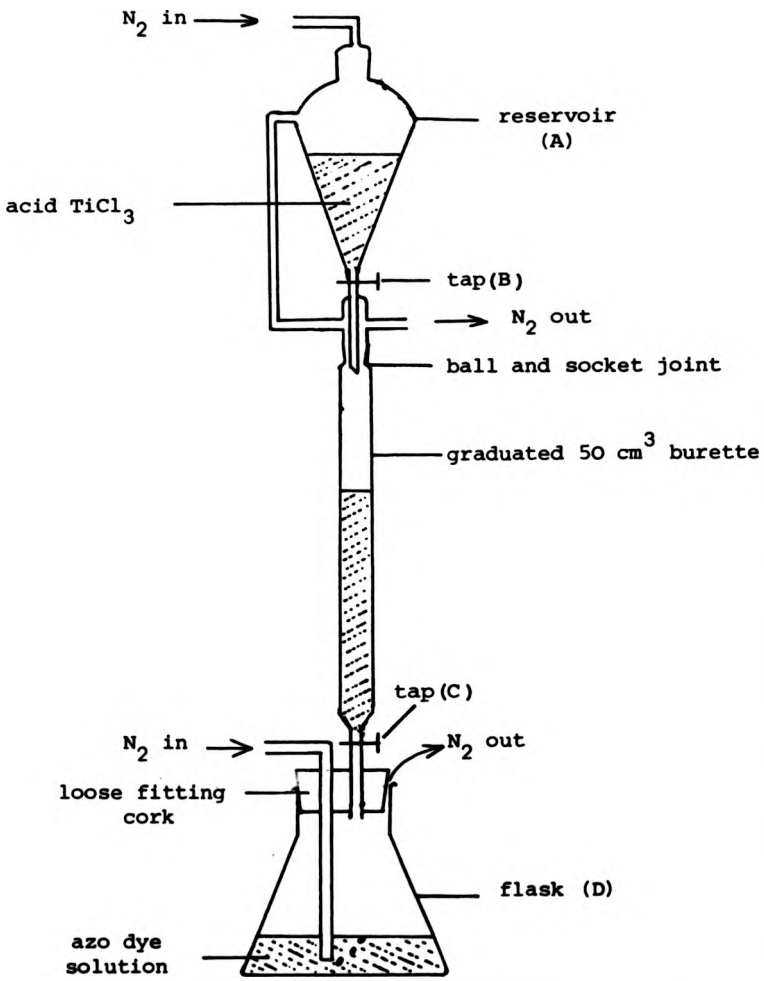
Apparatus for the determination of yields of azo dyes



mixture boiled for 5-10 minutes. The flask is cooled rapidly in ice, and 10% ammonium thiocyanate solution (2 cm^3) added. The remaining $TiCl_3$ is back-titrated with ferric ammonium sulphate solution (0.104 M), previously standardised iodometrically, and the end point observed by the appearance of red ferric thiocyanate. $TiCl_3$ is standardised by a similar titration.

Figure 17

Apparatus for the determination of yields of azo dyes



mixture boiled for 5-10 minutes. The flask is cooled rapidly in ice, and 10% ammonium thiocyanate solution (2 cm^3) added. The remaining $TiCl_3$ is back-titrated with ferric ammonium sulphate solution (0.104 M), previously standardised iodometrically, and the end point observed by the appearance of red ferric thiocyanate. $TiCl_3$ is standardised by a similar titration.

Problems:- It was found that the azo dye solutions prepared with certain couplers (in excess, as in all our kinetics studies) gave yellow-red solutions due to decomposed coupler after reduction with $TiCl_3$. Since the end-point is the appearance of a red colour, in most of these cases it was impossible to obtain accurate results and this method had to be abandoned. Potassium ferrocyanide was tried as an alternative to ammonium thiocyanate, and although the end-point was difficult to see, it was used to find the yield of dye from sodium 2,3-dihydroxynaphthalene-6-sulphonate and 4-chlorobenzenediazonium salts. Potassium dichromate as oxidant (with diphenylamine indicator) was also tried as an alternative to ferric ammonium sulphate, but was found to oxidise residual coupler.

Results:- Zollinger gives a percentage yield of 89.2% for the reaction between 4-chlorobenzenediazonium salts and sodium 2-hydroxynaphthalene-6-sulphonate. We obtained an average value from four separate experiments of 89.3% ± 5% which shows that our method gives reasonably accurate results (when the end-point is observable).

The only other azo dye to give a clear end-point in the titration, and hence a reasonable value for the yield, was that from the reaction of 4-chlorobenzenediazonium salts with sodium 2,3-dihydroxynaphthalene-6-sulphonate. The yield is 100.3% ± 0.2% from the average of four titrations. Bagal[88] also claims a yield of 100% for the coupling reaction between eight arenediazonium salts and dimethylaniline in non-aqueous media, and so we conclude that most relatively fast coupling reactions give yields of 100% azo product and so no corrections are normally required.

3. Results and Discussion

3.1 The structure of sodium syn-benzenediazotate-4-sulphonate

The debate about the structures of the two different forms of aryldiazotates has a long and celebrated history and is discussed in section 1.4.4. In view of the absence of definitive crystallographic material relating to the aryldiazotate, which would finally resolve the question, we have undertaken a low-temperature crystal structure determination of a syn-aryldiazotate. A considerable series of crystalline aryldiazotates were prepared, including the sodium and tetramethyl-ammonium salts of anti-4-nitrobenzenediazotate which crystallise as thin, irregular platelets which were unsuitable for X-ray crystallographic determination. The only suitable crystals which could be obtained were those of sodium syn-benzenediazotate-4-sulphonate (prepared as described in section 2.1.6).

3.1.1 Structure determination

The small needle-shaped crystals were found to decompose at room temperature in the X-ray beam. However, by cooling the crystal to -150°C using a Syntex LT-1 attachment, this problem was overcome. Unit cell dimensions and data were collected using a Syntex $P2_1$ four-circle diffractometer with a graphite monochromator. The small crystal size required that the initial orientation photograph was given only a partial rotation, and that all reflection centring was performed at slow speed.

Crystal Data

Stoichiometry = $C_6H_4N_2SO_4Na_2 3H_2O$;

Molecular weight = 348; Crystal type = monoclinic;

$\underline{a}$ = 5.559(1)Å, $\underline{b}$ = 11.699(4)Å, $\underline{c}$ = 19.371(4)Å;

$\alpha = \beta = \gamma = 90^{\circ}$; unit cell volume, $\underline{U}$ = 1259.9(6)Å^3;

Density, $\underline{D}$ = 1.30 g cm^{-3}; number of molecules in unit cell $\underline{Z}$ = 4;

Mo — Kα radiation; λ = 0.71069Å; F(000) = 616.

Accurate cell constants were obtained by means of least squares calculations based on the positions of 15 reflections. The systematic absence, 0 k l, $k + l \neq 2n$ and h o l, $h \neq 2n$, indicates either Pn a 2_1 or Pnam as the space group. The latter would require m or $\bar{1}$ symmetry for the molecule, and as these seem unlikely, the non-centrosymmetric space group was selected provisionally and shown to be correct by refinement. Since a very weakly diffracting crystal was used, data were collected slowly to achieve satisfactory accuracy. Reflections were measured using $\theta - 2\theta$ scans over a range $2\theta_{\alpha 1}$-0.8 to $2\theta_{\alpha 2}$+ 0.8 to a maximum 2θ of 45°. A variable scan rate of $0.5^{\circ} - 29.5^{\circ}$ min^{-1} was used, depending on the intensity of a preliminary 2s count. Background counts were recorded at the end of each scan for time equal to that of the scan. 1389 reflections were collected of which 838 were considered observed $[I/\sigma(I) \geq 3.0]$ and used in final refinement. Lorentz and polarisation corrections were applied, but, due to the small size of the crystal, not an absorption correction.

A Patterson synthesis revealed the position of sulphur (considered as a 'heavy' atom) and Fourier methods were applied to locate all the non-hydrogen atoms. Anisotropic temperature factors were used for the sulphur and sodium atoms in the last stages of least-squares refinement. Hydrogen atoms were not considered. The refinement converged to a final R of 0.62, with unit weights for all reflections.

Computing was carried out with the SHELX-76 program (except for the ORTEP diagrams which used XRAY-76) on a Burroughs B6700 computer. The final co-ordinates (courtesy of Dr N.A. Alcock) are listed in Table 9, interatomic bond lengths and angles in Table 10, skeletal torsional angles in Table 11 and intermolecular and interionic distances in Table 12. Anisotropic temperature factors, and observed and calculated structure factors, are listed in the appendix.

Table 9

Atomic Co-ordinates of the Bonded Atoms

(with standard deviations in parentheses)

ATOM	X	Y	Z
S	0.5009 (5)	0.5569 (2)	0.5000 (0)
O(1)	0.3553 (12)	0.4540 (6)	0.4984 (4)
O(2)	0.7308 (13)	0.5444 (6)	0.4652 (4)
O(3)	0.3665 (13)	0.6577 (6)	0.4774 (4)
O(5)	0.6326 (13)	0.6787 (6)	0.3339 (4)
O(6)	-0.3423 (14)	0.2975 (6)	0.4017 (4)
O(7)	0.3499 (20)	0.1945 (9)	0.7043 (6)
C(1)	0.5773 (19)	0.5765 (9)	0.5892 (5)
C(2)	0.4225 (20)	0.5364 (9)	0.6401 (6)
C(3)	0.4879 (19)	0.5523 (9)	0.7101 (5)
C(4)	0.7074 (19)	0.6047 (8)	0.7262 (6)
C(5)	0.8571 (20)	0.6459 (9)	0.6746 (6)
C(6)	0.7948 (20)	0.6325 (9)	0.6052 (6)
N(1)	0.7751 (17)	0.6322 (8)	0.7968 (5)
N(2)	0.8229 (16)	0.5500 (7)	0.8395 (5)
Na(1)	-0.0073 (7)	0.3820 (3)	0.4539 (2)
Na(2)	0.9937 (8)	0.6677 (3)	0.4054 (2)
O(4)	0.8078 (14)	0.4436 (6)	0.8176 (4)

Table 10

Interatomic Bond Lengths (Å) and Angles (°)

(with standard deviations in parentheses)

Bond Lengths

S	— C(1)	1.794	(10)
S	— O(1)	1.451	(7)
S	— O(2)	1.452	(8)
S	— O(3)	1.463	(8)
C(1)	— C(2)	1.390	(15)
C(1)	— C(6)	1.410	(15)
C(2)	— C(3)	1.416	(15)
C(3)	— C(4)	1.401	(15)
C(4)	— C(5)	1.387	(16)
C(5)	— C(6)	1.397	(16)
C(4)	— N(1)	1.455	(15)
N(1)	— N(2)	1.296	(13)
N(2)	— O(4)	1.318	(11)

Bond Angles

O(1)	— S —	C(1)	105.0	(5)
O(2)	— S —	C(1)	104.6	(5)
O(3)	— S —	C(1)	107.8	(5)
C(2)	— C(1) —	C(6)	122.1	(10)
C(3)	— C(2) —	C(1)	118.4	(10)
C(4)	— C(3) —	C(2)	119.6	(10)
C(5)	— C(4) —	C(3)	121.0	(10)
C(6)	— C(5) —	C(4)	120.3	(10)
C(3)	— C(4) —	N(1)	122.1	(10)
C(4)	— N(1) —	N(2)	119.2	(9)
N(1)	— N(2) —	O(4)	118.8	(9)

Table 10

Interatomic Bond Lengths (Å) and Angles (°)

(with standard deviations in parentheses)

Bond Lengths

S	—	C(1)		1.794 (10)
S	—	O(1)		1.451 (7)
S	—	O(2)		1.452 (8)
S	—	O(3)		1.463 (8)
C(1)	—	C(2)		1.390 (15)
C(1)	—	C(6)		1.410 (15)
C(2)	—	C(3)		1.416 (15)
C(3)	—	C(4)		1.401 (15)
C(4)	—	C(5)		1.387 (16)
C(5)	—	C(6)		1.397 (16)
C(4)	—	N(1)		1.455 (15)
N(1)	—	N(2)		1.296 (13)
N(2)	—	O(4)		1.318 (11)

Bond Angles

O(1)	—	S	—	C(1)		105.0 (5)
O(2)	—	S	—	C(1)		104.6 (5)
O(3)	—	S	—	C(1)		107.8 (5)
C(2)	—	C(1)	—	C(6)		122.1 (10)
C(3)	—	C(2)	—	C(1)		118.4 (10)
C(4)	—	C(3)	—	C(2)		119.6 (10)
C(5)	—	C(4)	—	C(3)		121.0 (10)
C(6)	—	C(5)	—	C(4)		120.3 (10)
C(3)	—	C(4)	—	N(1)		122.1 (10)
C(4)	—	N(1)	—	N(2)		119.2 (9)
N(1)	—	N(2)	—	O(4)		118.8 (9)

Table 11

Skeletal Torsional Angles (°)

(with standard deviations in parentheses)

C(3) — C(4) — N(1) — N(2)	69.1 (13)
O(1) — S — C(1) — C(2)	-28.6 (10)
O(2) — S — C(1) — C(2)	-148.2 (11)
O(3) — S — C(1) — C(2)	91.2 (9)
C(2) — C(3) — C(4) — N(1)	174.6 (9)
C(6) — C(5) — C(4) — N(1)	-174.2 (9)

Table 12

Intermolecular and Interionic Distances (Å)

(with standard deviations in parentheses)

Sodium Co-ordination

Na(1) — O(1)	2.349 (8)
Na(1) — O(6)	2.338 (9)
Na(1) — O(6)	2.505 (8)
Na(1) — O(2)	2.404 (8)
Na(1) — N(2)	2.568 (10)
Na(2) — O(2)	2.442 (8)
Na(2) — O(3)	2.501 (8)
Na(2) — O(3)	2.573 (8)
Na(2) — O(3)	2.573 (8)
Na(2) — O(4)	2.410 (9)
Na(2) — O(5)	2.442 (9)
Na(2) — O(5)	2.397 (8)

Hydrogen Bonding

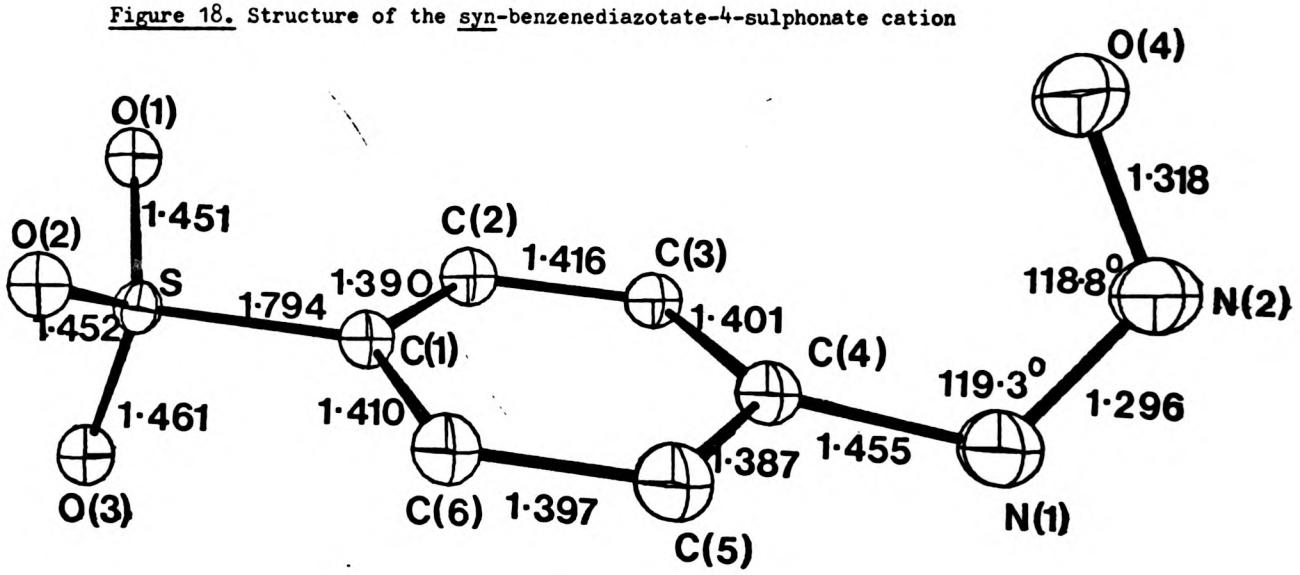
N(1) — O(6)	2.830 (12)
O(6) — O(6)	2.994 (11)
O(5) — O(7)	2.918 (14)
O(4) — O(5)	2.853 (11)
O(4) — O(7)	2.735 (14)

3.1.2 Discussion of results

(i) The molecule (Fig. 18), was found to have the conventionally accepted structure [138] with the syn-diazotate group in a cis configuration, and consequently the suggestion that the syn form has a trans configuration [127] is incorrect. The dimensions of the sulphonate group are almost identical to those in benzenediazonium-4-sulphonate [180], although the benzene ring is less distorted. This would be expected as the diazotate group is a much weaker electron-withdrawing substituent than the diazonium group . Kübbler and Luttke [138] predicted from the infra-red spectra of a series of substituted aryldiazotates that the syn-aryldiazotate has a non-planar structure and, by comparison with compounds having isoelectronic groups, that the syn-diazotate group is cisoid and distorted in some unspecified way. The C(4) — N(1) bond makes a slight angle (5.5 (9)°) with the plane of the ring and the diazotate group (itself planar), has a dihedral angle of 69.1 (13)° with the ring plane. Comparison with the crystal structure of potassium syn-methyldiazotate [141] shows significant differences, i.e. (a) N(1) — N(2) and N(2) — O(4) in the aromatic compound are fairly similar, 1.296(13) Å and 1.318(11) Å respectively whereas in the aliphatic diazotate they are substantially different, i.e. 1.246(8) and 1.306(7) Å respectively. This indicates more extensive delocalisation in sodium syn-benzenediazotate-4-sulphonate, viz.

(b) The angle C(4) — N(1) — N(2) (119.2(9)°) in the aryldiazotate is significantly closer to pure sp^2 than the in aliphatic compound (116.2(5)°) whereas the angles N(1) — N(2) — O(4) are fairly similar (118.8(9)° and 119.8(5)°).

Figure 18. Structure of the syn-benzenediazotate-4-sulphonate cation



(ii) Crystal packing (Fig. 19)

The anions, cations and water molecules are extensively bonded to give a rigid 3-dimensional structure.

Na(1) is five-coordinated to O(1), O(2) and N(2) of the anion and also to two O(6) water molecules. Na(2) is six-coordinated to O(2), O(3) twice and O(4) of the anion and to two O(5) water molecules. The N(1) — O(6) distance (2.830(12) Å) indicates the presence of a hydrogen bond. O(6) water molecules are also connected to each other in a chain throughout the structure probably by hydrogen bonds. Similarly, O(4) of the anion is doubly hydrogen-bonded to water molecules O(5) and O(7). Finally, there is a hydrogen bond between O(5) and O(7).

3.2 The Coupling Reaction

3.2.1 The influences of ring-substituents on the coupling rate constants of arenediazonium cations with sodium 2,3-dihydroxynaphthalene-6-sulphonate

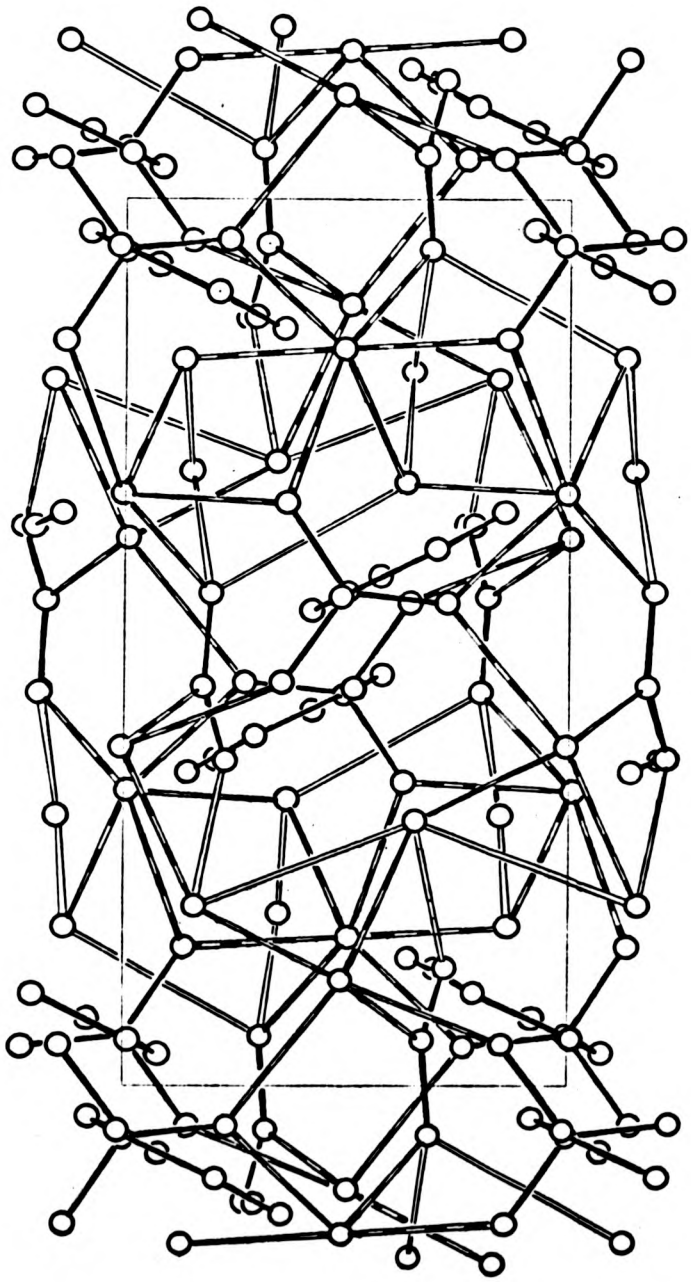
In ref. 99, the kinetics of reaction of a series of substituted arenediazonium cations with sodium 2,3-dihydroxynaphthalene-6-sulphonate (XXX) at pH 5.6 and 9.9 were studied and the two Hammett plots thus obtained were reported to be reasonably linear. We have measured the rate constants of this reaction including in addition very reactive arenediazonium cations (e.g. the 4-nitro compound at pH 9.9) and also one very inert species, i.e. the 4-amino compound at pH 5.6.

Equation 80, p. 79 was used to find the absolute rate constant, denoted k_{A1}, for the coupling of 100% singly ionised coupler with the arenediazonium salts from the rate constants measured at pH 5.6. The contribution to the apparent rate constants, measured at pH 9.9, from doubly ionised form of the coupler was calculated (89)

$$k_{DA} = k_{A9.9} - k_{A1} \qquad (89)$$

where k_{DA} is the rate constant due to the doubly ionised species, $k_{A9.9}$

Figure 19. Crystal packing in disodium syn- benzenediazotate-4-sulphonate



is the apparent rate constant at pH 9.9 and k_{A1} is defined above. Subsequently the absolute rate constants of the coupling of a series of arenediazonium ions with 100% doubly-ionised coupler, denoted k_{A2}, were calculated from an equation similar to (80), viz.

$$k_{A2} = k_{DA} + pK_{A2} - pH \qquad (90)$$

The values of the apparent rate constants at pH 5.6 and at pH 9.9 and also of k_{A1} and k_{A2} (including the data from ref. 99) are given in Table 13.

Table 13

Compiled rate constants for the coupling reaction between substituted arenediazonium cations and sodium 2,3-dihydroxynaphthalene-6-sulphonate

Substituents	log $k_{A5.6}$ ($k_{A5.6}$ = apparent rate constant at pH 5.6)	log $k_{A9.9}$ ($k_{A9.9}$ = apparent rate constant at pH 9.9)	log k_{A1}	log k_{A2}
4 $-N(CH_3)_2$	-	0.45	-	-
4 - NH_2	- 5.2 ± 1	0.99	-2.5±1	3.22±1
4 - CH_3O	- 0.55	2.88	2.09	5.03
3,5 - $(CH_3)_2$	-	3.55	-	-
4 - CH_3	0.212	3.78	2.85	5.96
3 - CH_3	0.826	3.94	3.47	6.00
none	0.829	4.18	3.47	6.32
3 - CH_3O	1.05	4.63	3.69	6.81
4 - F	1.26	4.63	3.90	6.77
4 - Cl	1.52	4.77	4.16	6.88
3 - Cl	2.13	5.01	4.78	6.85
3,4 - Cl_2	2.59	4.97	5.23	-
4 - CN	2.97	5.54 ± 0.5	5.61	-
3 - NO_2	3.14	5.61 ± 0.5	5.78	-
4 - NO_2	3.25	5.55 ± 0.5	5.89	-

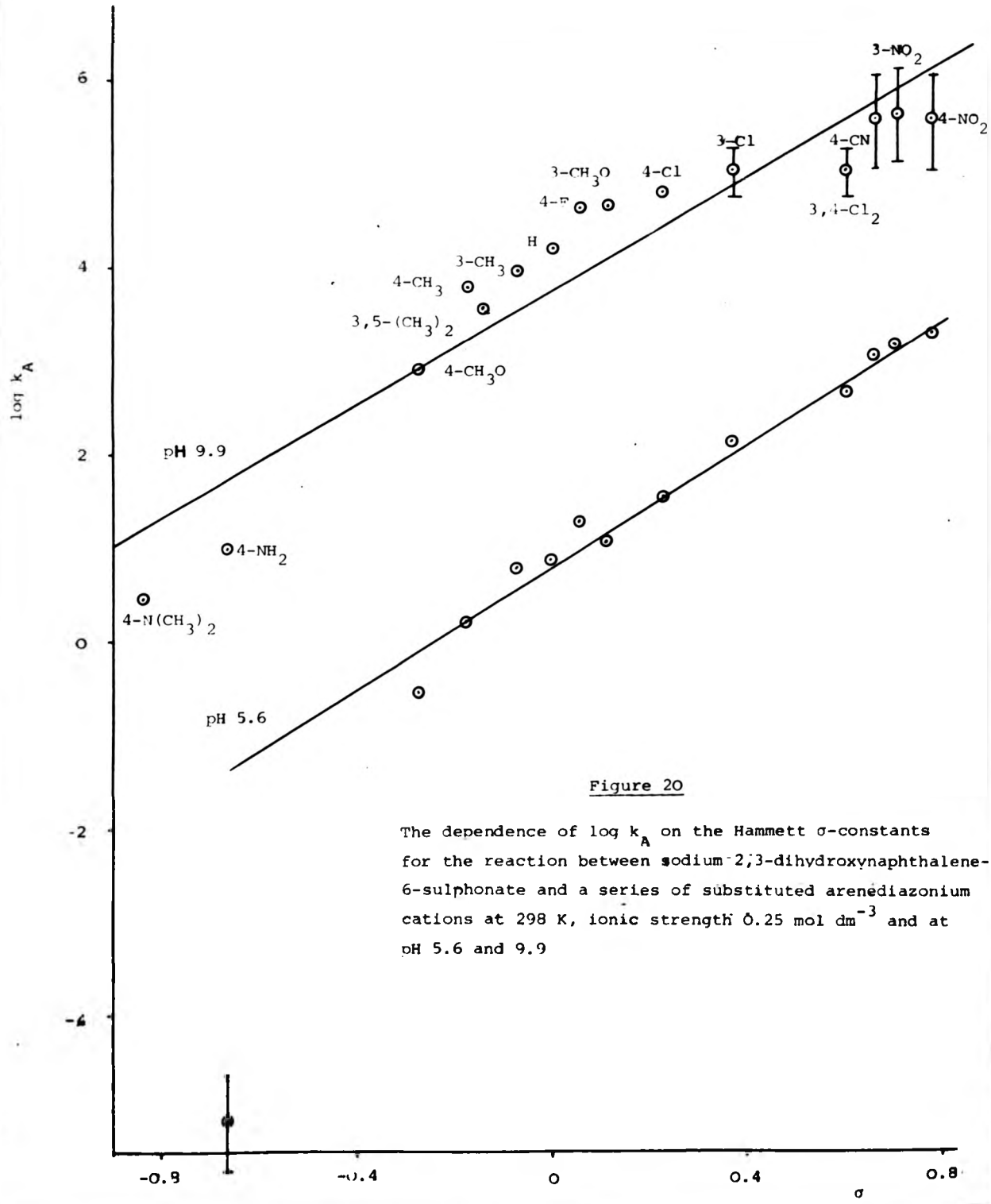


Figure 20

The dependence of log k_A on the Hammett σ-constants for the reaction between sodium 2,3-dihydroxynaphthalene-6-sulphonate and a series of substituted arenediazonium cations at 298 K, ionic strength 0.25 mol dm^{-3} and at pH 5.6 and 9.9

The values of log $k_{A5.6}$ (and log k_{A1}) from the reaction of the coupler with arenediazonium salts without strongly-electron donating substituents, e.g. 4-NH_2, gave a reasonable correlation with the Hammett σ-constants (Fig. 20). The reaction of the 4-amino component with the coupler at pH 5.6 is extremely slow with $t_{\frac{1}{2}}$ of the order of days and so the dye formation was recorded for much less than one half-life and as a result, the accuracy of the resulting rate constants is low but is expected to be within a factor of 10, i.e. log $k_{A5.6}$ < ± 0.5. This correlation, presented in Fig. 20, includes data from some di-substituted arenediazonium ions when the σ-constants are summed[100]. Excluding the deviant point for 4-NH_2, the correlation coefficient is 0.987 and the Hammett ρ values is 3.31(S.D. = 0.17).

The apparent rate constants measured at pH 9.9 include contributions from both the singly ionised coupler and a small quantity of the more reactive doubly ionised species, and so log $k_{A9.9}$ should exceed log k_{A1} in Fig. 20, which it does except for the values for the reaction of the four most reactive arenediazonium cations with the coupler. The latter four rate constants are prone to inaccuracy as the reaction rate is near to the limit of the mixing time of the stopped-flow apparatus ($t_{\frac{1}{2}}$ = ca. 5 ms) and so these values of log $k_{A9.9}$ were estimated to be accurate to ±0.5 units (it was noted that an increase of only 0.5 in the values of log $k_{A9.9}$ of the four data points at σ ≥ 0.6 gave more reasonable values for k_{A2}). The data measured at pH 9.9 were found to correlate only poorly with the Hammett σ-constants (Fig. 20) to yield ρ = 3.06 (S.D. = 0.29) with a correlation coefficient of 0.946. The poor fit is possibly due to (a) the rate constants $k_{A9.9}$ from those arenediazonium ions with substituents having σ ≥ 0.6 are inaccurate, the true values being somewhat larger (with larger values, this correlation at pH 9.9 is not dissimilar to that at 5.6) and (b) 'through conjugation'

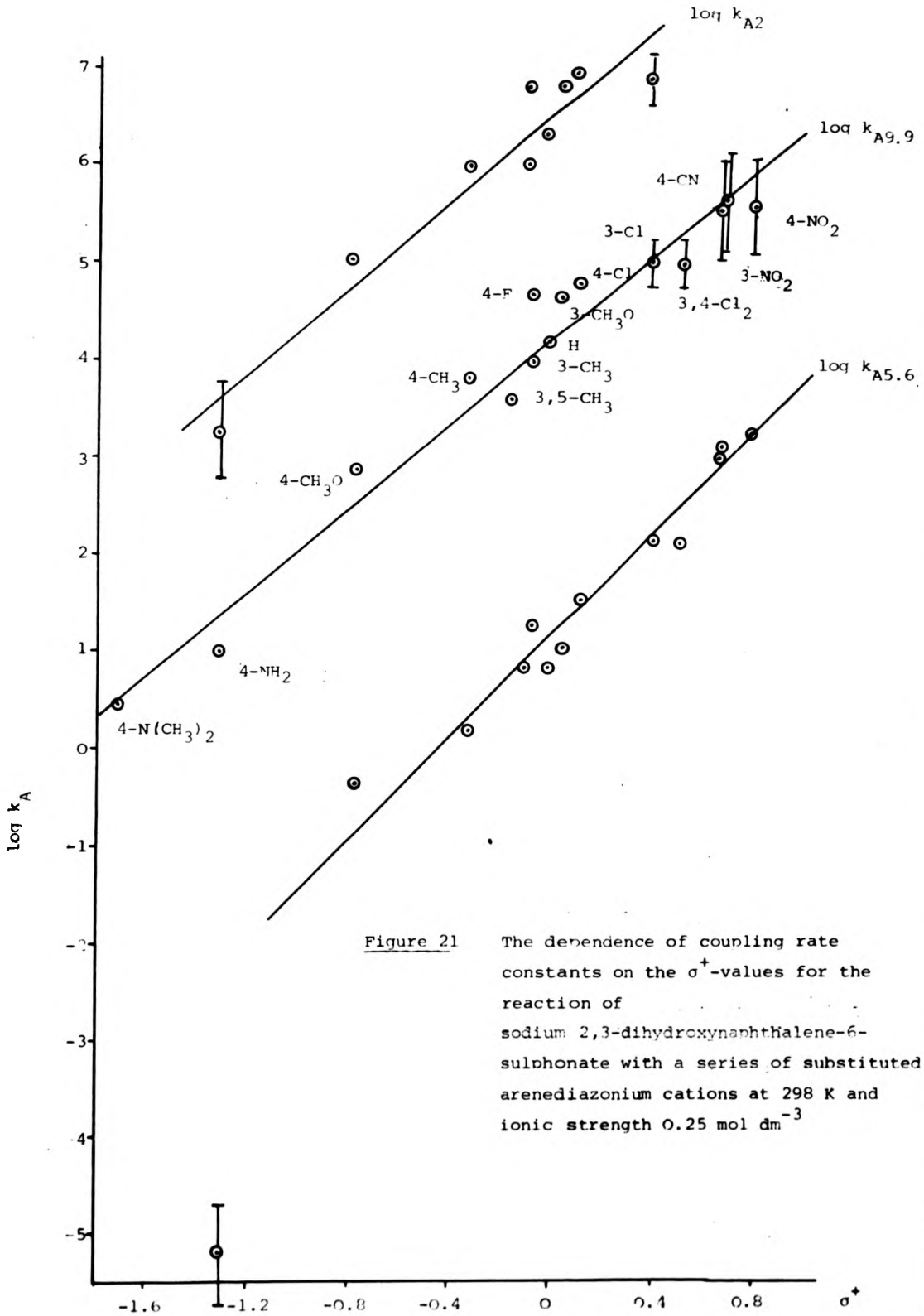
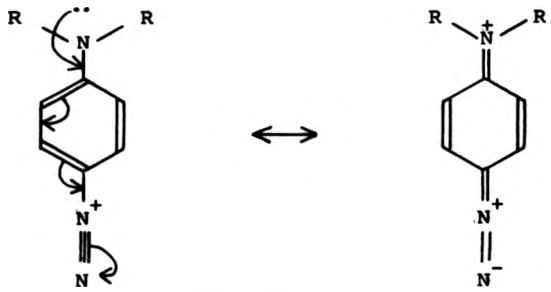


Figure 21 The dependence of coupling rate constants on the σ^+-values for the reaction of sodium 2,3-dihydroxynaphthalene-6-sulphonate with a series of substituted arenediazonium cations at 298 K and ionic strength 0.25 mol dm^{-3}

between the strongly electron-donating substituents and the diazonium group (91) giving lower rate constants than expected.



(91)

Under these circumstances, the σ^+ substituent constants may give a better correlation. Taft [133] recommends the use of σ^+_R substituent constants when the reaction site is strongly electron-withdrawing (as is the diazonium group) and he successfully used his dual parameter equation with these values and Zollinger's data for the reaction between a series of substituted arenediazonium salts and 2-naphthylamine-6-sulphonic acid [98]. The correlation between log $k_{A5.6}$ and the σ^+ substituent for the data measured at pH 5.6 (Fig. 21) was only slightly better than the correlation obtained with the simple Hammett σ-constants. A gradient of $\rho = 2.61$ (S.D. = 0.14) and almost the same correlation coefficient = 0.985 were calculated. A much improved correlation (of 0.981) was found for the data measured at pH 9.9 with the σ^+ constants; $\rho = 2.134$ (S.D. = 0.118), which implies that a degree of through conjugation occurs as in (91). The contribution to the apparent rate constants $k_{A9.9}$ from the doubly ionised species was evaluated and used to correlate log k_{A2} with σ^+ as described above: this plot is also given in Fig. 21. Obviously, the value of k_{A2}, where $\sigma^+ > 0.5$, could not be calculated but in general, the doubly-ionised form is ca. 300 - 500 fold more reactive than its singly ionised counterpart. The plot is roughly linear with $\rho = 2.22$ (S.D. = 0.25) and has a correlation coefficient = 0.959.

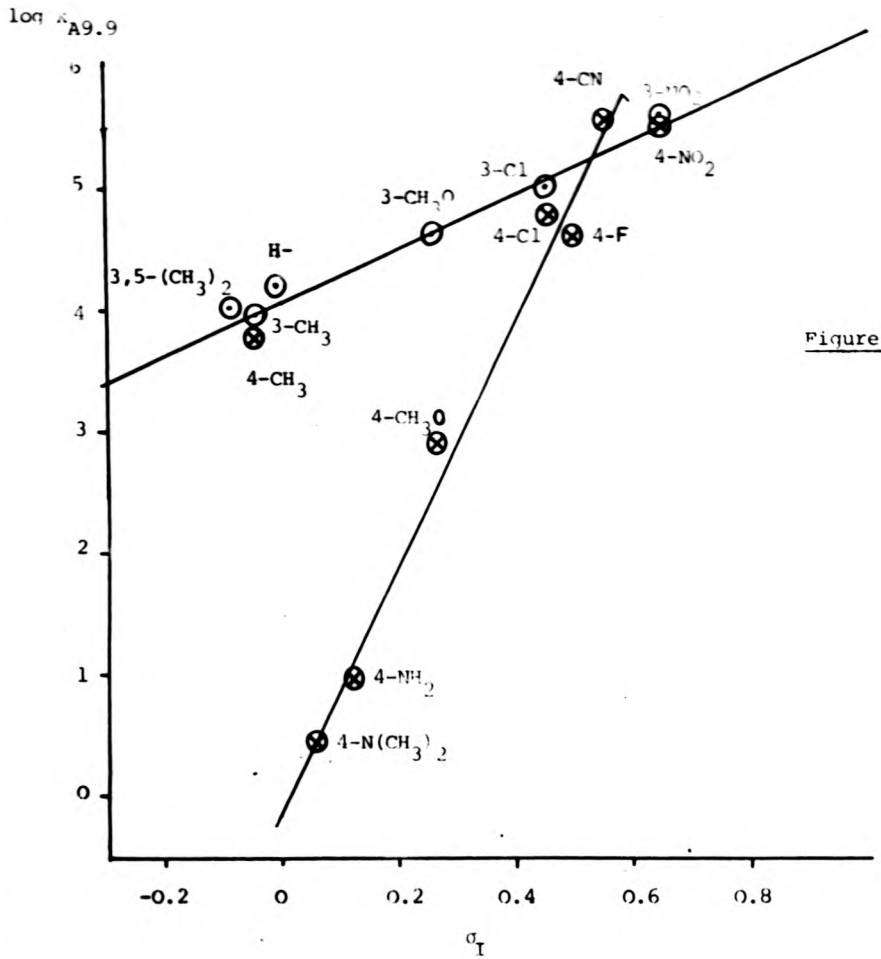
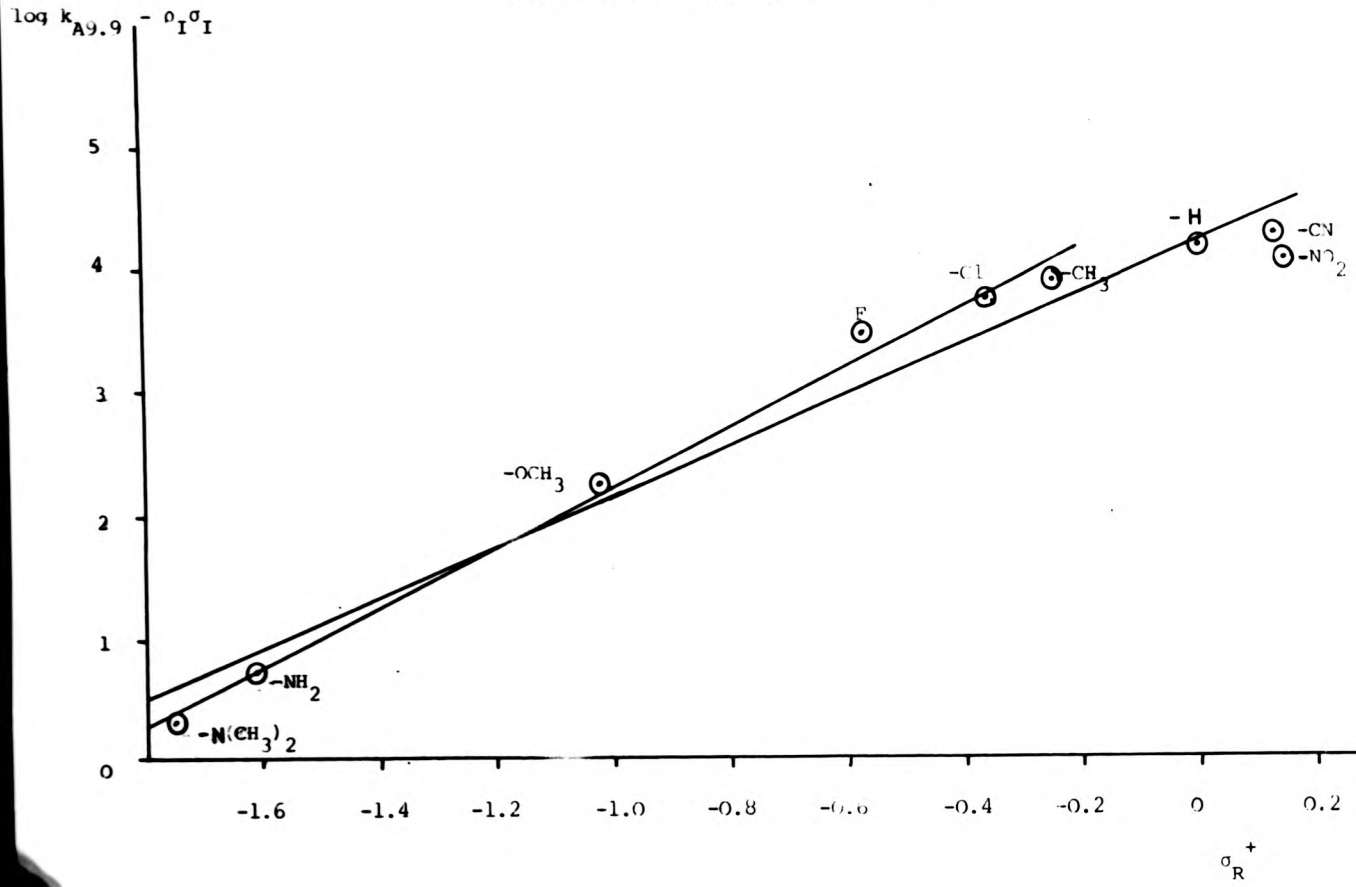


Figure 22 Plots of log $k_{A9.9}$ versus σ_I for the reaction between 3-substituted (⊙) and 4-substituted (●) arenediazonium cations with sodium 2,3-dihydroxynaphthalene-6-sulphonate at pH 9.9

Figure 23 Graph of log $k_{A9.9} - \rho_I\sigma_I$ versus σ_R^+ for the reaction between 4-substituted arenediazonium cations and sodium 2,3-dihydroxy-naphthalene-6-sulphonate at pH 9.9



The gradients of the three plots of log (rate constants) against σ^+ in Fig. 21 lie within a range of ca. 2.1 - 2.6 which indicates that the effect of substitution on the arenediazonium salt is approximately the same for the reaction with the mono-ionised coupler as with the doubly-ionised form. The size of the ρ values indicates that the ring subtituents do not have a large effect on the rate of reaction, which is as generally expected for relatively rapid reactions. The positive ρ value suggests that the reaction site, i.e. the diazonium group, increases its electron density during the reaction, which confirms equation (35), p21, as the most likely reaction pathway. The σ^+ values are required because the effect of the 'through conjugation' is to reduce the electron density of the diazonium group and so directly increase its reactivity towards negatively charged species such as the couplers. This activation is supplementary to the effect of the substituted benzene ring which alone would give a rate constant which may be correlated against σ^o substituents constants.

Taft [133] successfully correlated one coupling reaction (see above) to his σ_R^+ substituent constants in the dual parameter equation (68), which is repeated here [133]:

$$\log (k_X / k_H) = \sigma_I \rho_I + \sigma_R^+ \rho_R \qquad (68)$$

To test the validity of this approach we have utilised (68) for this reaction. The correlation between log $k_{A9.9}$ and σ_I for the reactions involving 3- and 4- substituted arenediazonium cations and between log $k_{A9.9}$ - $\rho_I\sigma_I$ and σ_R^+ [133] for those arenediazonium cations with 4-substituents are given in Figs. 22 and 23 respectively. The data from the reactions with 3-substituted arenediazonium cations gave an excellent correlation with σ_I and from the six data points, a correlation coefficient of 0.997 and ρ_I = 2.235 (S.D. = 0.170) were calculated which compares Taft's figure of ρ_I = 3.994 from a similar

coupling reaction [98]. The reaction constant ρ_I was then applied to the data for the 4-substituted compounds to derive ρ_R = 2.085 (S.D. = 0.153) with a correlation coefficient of 0.982 from the nine data points. If, however, the three data points from the reactions of the coupler and the unsubstituted, the 4-cyano and the 4-nitrobenzenediazonium cations are omitted, a much better correlation is found with ρ_R is 2.439 (S.D. = 0.115) and the correlation coefficient is 0.996. (Taft's value of ρ_R from the coupling reaction of 2-naphthylamine-6-sulphonic acid and a series of arenediazonium salts is 2.522)[98]. The data from the reactions followed at pH 5.6 did not give a very good correlation with (68) and were not considered further.

The low values of log k_{A2} for the reaction of 4-cyano and 4-nitrobenzenediazonium ions with coupler, (Fig. 23), may possibly be attributed to the inaccuracy inherent in their measurement (see above); however, this is unlikely to be the reason for the data point for the coupling of the unsubstituted compound. The competing reaction of the arenediazonium cation with OH^- to give aryldiazotates may possibly explain this discrepancy. The theoretical rate constant k_{A2} of the reaction between the doubly-ionised coupler and 4-nitrobenzenediazonium cations was found by extrapolation of the plot in Fig. 21 which gave a value of ca. 10^8 dm^3 $mol^{-1}s^{-1}$. The rate constant (k_1) for the formation of syn-4-nitrobenzenediazotate is 5×10^5 dm^3 $mol^{-1}s^{-1}$ (from section 3.3). Therefore the relative rates of the three competing reactions of 4-nitrobenzenediazonium cation at pH 9.9 are as follows:

Rate of azo dye formation from the mono-ionised coupler = k_{A1}[coupler] $\sim 3 \times 10^5 \times 0.002 = \underline{6 \times 10^2 s^{-1}}$

Rate of azo dye formation from the doubly-ionised coupler = k_{A2}[coupler] $\sim 10^8 \times 0.002 \times 0.0067$
$= \underline{1.34 \times 10^3 s^{-1}}$

Rate of aryldiazotate formation = $k_1[OH^-] \sim 5 \times 10^5 \times 10^{-4} = \underline{50s^{-1}}$

(N.B. 0.002 is a typical coupler concentration, the factor of 0.0067 accounts for the proportion of the total concentration of the coupler present as the doubly-ionised form and $[ArN_2^+]$ is approximately the same in each case and so omitted). However, since the rates of azo dye formation from either the mono- or doubly-ionised forms of the coupler are appreciably greater than the rate of aryldiazotate formation, the latter does not account for the deviant point.

One explanation for the slight curvature of Fig. 23 may be that Taft's dual parameter equation [133] utilising the σ_R^+ substituent constants does not fully account for the substituent effects in this reaction. An alternative possibility is that the rate constants for step (35) approach those of step (34) for the most reactive arenediazonium compounds and so a change in the rate-determining stage occurs with the resultant drop in the value of ρ as σ_R^+ increases. To confirm the latter explanation, however, further experiments involving possibly base catalysis by pyridine and the detection of a hydrogen isotope effect are required.

3.2.2 The influence of the nature of the coupler on the coupling rate constant

For comparative purposes, all couplers were reacted with the same arenediazonium salt, i.e. 4-chlorobenzenediazonium tetrafluorborate. This particular example was chosen because of its relative stability at room temparature and in daylight and its purity of ca. 98% and also because it reacts with most of the relevant couplers at a convenient rate.

The couplers are divided into three groups (see section 2.3.1 (i)) and are dealt with separately here.

(i) Hydroxynaphthalene compounds

The second order, and where the pK_A is known, absolute rate constants for the reactions of 4-chlorobenzenediazonium tetrafluoroborate with ten hydroxynaphthalene couplers are listed in Table 14. Three of the rate constants were taken from ref. 99 and are included for comparative purposes.

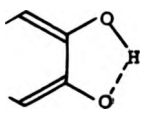
Table 14

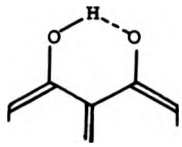
Stoichiometric(k_s) and absolute(k) second-order rate constants for the reaction of 4-chlorobenzenediazonium cation with selected couplers

Coupler	pH	k_s /$dm^3 mol^{-1} s^{-1}$	log k
2-Naphthol (XXVI)	4.57	1.42	5.49
	5.70	19.0	5.32
	6.77	133	5.26
			Average = 5.36
2-Naphthol-6-sulphonic acid (XXVII)	5.60	153	3.54
2-Naphthol-7-sulphonic acid (XXVIII)	5.60	3.23	3.38
2,3-Dihydroxynaphthalene (XXIX)	4.57	7.70	5.27
	5.73	50.2	4.92
	5.86	122	5.18
	6.06	177	5.14
	6.75	398	4.98
			Average = 5.10
2,3-Dihydroxynaphthalene-6-sulphonic acid (XXX)	5.60	33.2	4.16
2,7-Dihydroxynaphthalene (XXXI)	5.69	29.3	4.48
	4.57	2.25	4.48
	6.06	39.7	4.42
	7.31	988	4.56
			Average = 4.47
2,7-Dihydroxynaphthalene-3,6-disulphonic acid (XXXII)	5.69	6.64	4.05
	4.57	0.992	4.35
	6.06	19.0	4.14
			Average = 4.18
1,8-Dihydroxynaphthalene (XXXIII)	5.69	7.05×10^4	5.55
	5.30	3.20×10^4	5.55
	4.33	3.42×10^3	5.55
			Average = 5.55
1,8-Dihydroxynaphthalene 3,6-disulphonic acid (XXXIV)	2.86	13.7	2.10
	4.57	46.0	1.94
	5.15	0.57	2.43
			Average = 2.16
1,5-Dihydroxynaphthalene	5.82	1660	-

2-Naphthol (XXVI) couples to arenediazonium salts in the 1-position as a result of strong activation of this position by the $-O^-$ group. The effect of substitution by further hydroxyl groups or by sulphonate groups is to modify its coupling ability by mesomeric activation, inductive deactivation and steric hindrance effects.

The effect of a second unionised hydroxyl group in the 3-position (XXIX) is to reduce log k by 0.26 and in the 7-position (XXXI) by 1.18. The depression of log k by the hydroxyl group is mainly due to deactivation by inductive withdrawal of electrons. The hydroxyl group in the 3-position has apparently a much smaller effect than in the 7-position, which is possibly due to activation of the coupling carbon atom caused by hydrogen bonding between the adjacent 2- and 3- hydroxyl groups. This phenomenon is also found with (XXXIII) and is reflected by the relatively large value of log k = 5.55, i.e.



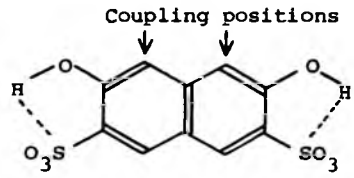


Sulphonate groups reduce the coupling ability of the coupler both by inductive withdrawal and steric hindrance effects and this is clearly demonstrated in Table 14.

The effect of substitution of a sulphonate group in the 6- or 7- positions of (XXVI) is to reduce log k by 1.83 and 1.98 respectively. The depression of log k by the smaller values of 0.94 on substitution of (XXIX) by a 6-sulphonate group to give (XXX) may be due to hydrogen bonding between the $-O^-$ group and the adjacent hydroxyl group.

Substitution by two sulphonate groups would be expected to have a larger deactivating effect than a single group as in (XXX).

However, the decrease in log k from (XXXI) to (XXXII) is only 0.29. The effect of the sulphonate groups may be complicated by hydrogen bonding between the sulphonate groups and the adjacent hydroxyl groups, as in (XXXV).



(XXXV)

Although (XXXIII) is slightly more reactive than (XXVI), the effect of two sulphonate groups in the 3- and 6- positions is the relatively large depression of log k from 5.55 to 2.16 reflecting both electronic deactivation of the coupling positions and sterically hindering the approach of the incoming electrophile to either the 2- or 4- positions.

The hydroxyl group itself has a small electronic effect (usually deactivation) on the reactivity of the coupler by both inductive withdrawal and mesomeric release of electronic charge. At high pH, however, the hydroxyl group is ionised to $-O^-$ which is a strongly activating substituent by mesomeric release of electrons. The absolute rate constant for the reaction of the doubly-ionised form of (XXX) with the 4-chlorobenzenediazonium cation has been calculated to be 7.59×10^6 mol dm^{-3} s^{-1} (see section 3.2.1) which is substantially higher than the corresponding rate constant of the coupling of the compound with only one hydroxyl group, i.e. (XXVII).

(ii) 2,3-Dihydroxynaphthalene - metal ion complexes

The insolubility of these compounds in water at low pH made the measurement of their pK_A values impossible, and therefore only apparent second-order rate constants are given in Table 15. 2,3-Dihydroxynaphthalene has the trivial name 'Dinol' which is used

in reprographic literature and will be referred to as such here.

Table 15

Second-order rate constants (k_2) for the coupling reaction of 2,3-dihydroxynaphthalene - metal ion complexes with 4-chlorobenzenediazonium tetrafluoroborate

Reaction	Coupler	pH	k_2 ($dm^3 mol^{-1} s^{-1}$)
(a)	Dinol-Niobate	6.93	5.17×10^3
		8.67	4.66×10^4
		9.34	5.52×10^4
		10.7	3.48×10^4
(b)	Dinol-Molybdate	8.77	2.42×10^4
		11.20	1.08×10^5
(c)	Dinol-Tantalate	8.77	2.42×10^4
		10.83	1.19×10^5
(d)	Dinol-Borate	5.90	63.9
		8.63	10^3
		8.67	5.37×10^3
		10.26	1.23×10^4

Dinol-niobate, tantalate and molydbate are structurally similar and so reactions (a) - (c) will be dealt with together below. Microanalysis of both 'dinol-borate', recrystallised from water, and its dye from coupling with 4-chlorobenzenediazonium tetrafluoroborat indicated that both samples had less than 0.5% boron. Presumably, on dissolving dinol-borate in water, it dissociates to 'dinol' and boric acid by equilibrium (96) discussed in section 3.2.3. The rate constants

for (d) given in Table 15 are therefore not for the reaction of the arenediazonium cation with 'dinol-borate', but for the reaction with free 'dinol' (once corrected for the differences in molecular weight).

The coupling rate constants of reactions (a) - (c) demonstrate that they are pH dependent which is because a rise in pH results in an increased concentration of the reactive ionised form of the coupler giving a corresponding increase in the rate constant. The values of k_2 from reaction (a) at and above pH 8.67 are approximately the same, which indicates that ca. pH 8.7 is greater than the pH equivalent to the pK_A value of 'dinol-niobate' and therefore the rate constants at pH $\geq$ 8.7 are equal to the absolute rate constant. Hence k was calculated as the average of the three values of k_2 measured between pH 8.67 and pH 10 .7. The pK_A values were assumed to be less than a value of 10.8 because an approximately one hundred-fold increase in $[OH^-]$ above pH 8.77 results in only a four-fold increase in rate constant (and therefore the pK_A value lies between 8.77 and 10). The rate constants at pH 11.20 and pH 10.83 from reactions (b) and (c) respectively were therefore considered as the absolute rate constants k. The absolute rate constants from reactions (b) and (c) are similar which suggests that Mo(V) and Ta(V) affect equally the coupling ability of (XXIV). However, since they are in neither the same group nor series of the periodic table, this is probably merely a coincidence. There is only a small difference between the rate constants for reaction (c) and (a) which would be expected as niobium (V) and tantalum(V), being in the same transition metal group and because of the lanthanide contraction, have very similar properties.

(iii) Couplers having an amide group

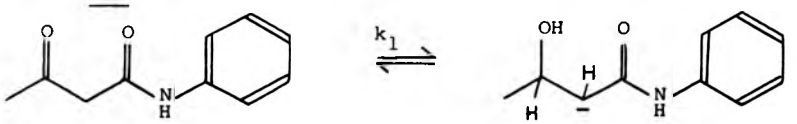
Certain amide couplers were found to couple with arenediazonium salts (Table 16), albeit by a variety of mechanisms.

Table 16

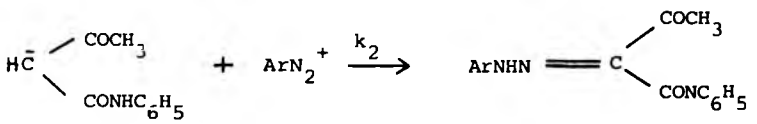
The rate constants for the coupling of aromatic amides with arenediazonium salts

Coupler	Ring substituents on ArN_2^+	pH	$k(dm^3 mol^{-1} s^{-1})$
Acetoacetanilide	2,5-diethoxy-4-tolythio	7.34	2.4×10^3
N-Benzylacetamide	"	7.34	2.4×10^3
2-Hydroxy-3-(N-2-methylphenyl)-naphthamide	"	7.34	5.36
	4-chloro	7.48	3.5×10^4
N-methylbenzamide	"	7.32	36.2

The kinetics of coupling acetoacetanilide with a series of substituted arenediazonium salts has been investigated by Sterba et al [18] who used the Yukawa-Tsuno equation [150] to demonstrate a linear dependence of rate constant on σ and proposed a two-step reaction mechanism viz.



(92)



(93)

$k_1 = 9.2\ s^{-1}$ and k_2 is the rate determining step.

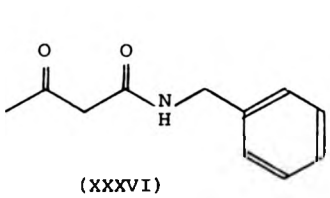
To obtain our rate constants k we have used their equation (94).

$$k = k_A([H^+] + K_A) \Big/ K_A[\text{Acetoacetanilide}] \qquad (94)$$

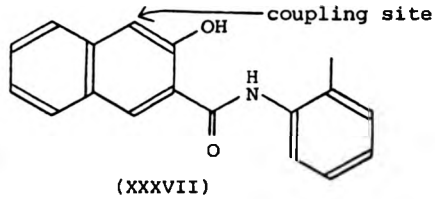
where k_A = the experimental pseudo-first order rate constant

K_A = dissociation constant of acetoacetanilide = 10^{-10}.

As would be expected from the similarity in structure, benzylacetoacetamide (XXXVI) couples with the arenediazonium cations with almost the same rate constant as acetoacetanilide itself.



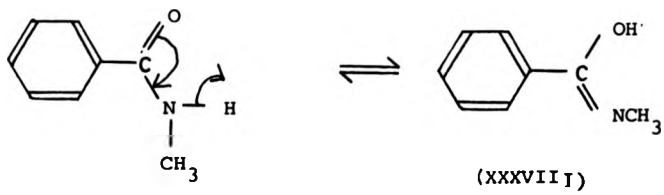
(XXXVI)



(XXXVII)

2-Hydroxy-3-(N-2-methylphenyl)-naphthamide (XXXVII) couples as a result of activation of the 1- position by the 2-hydroxyl group.
The 2,5-diethoxy-4-tolylthiobenzenediazonium cation was chosen because of its interest in the dyeline reprographic process [182].

N-methylbenzamide, unlike other similar compounds such as benzamide, N,N-dimethylbenzamide and DMF, couples with arenediazonium salts at pH 7.3 probably because it has both a labile proton and the stabilizing effect of the methyl group which appears to be required to obtain a suitably activated species, i.e. possibly (XXXVIII) which may react by N- coupling.

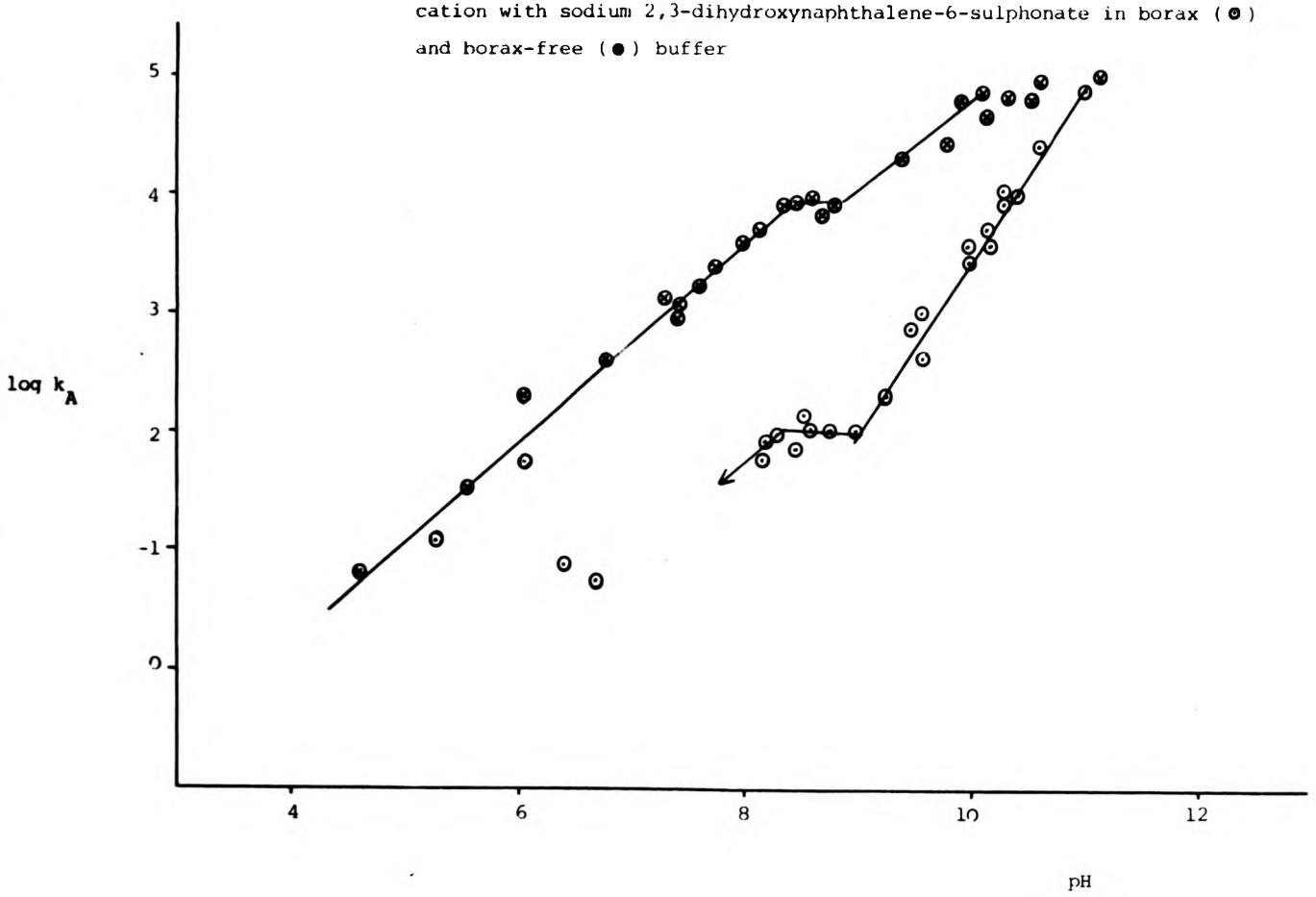


(95)

(XXXVIII)

Amides hydrolyse slowly in both acidic and basic solutions and so we have measured the rate constants at only ca. pH 7. Small pH changes hardly affected k_A for the reaction of acetoacetanilide with 4-chlorobenzenediazonium cations as found by Sterba [181], because the activating hydroxyl group of the enol isomer is fully ionised in the pH range utilised.

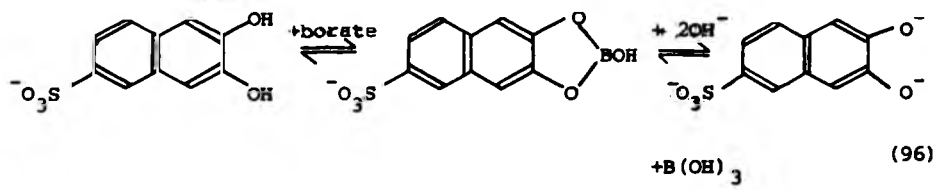
Figure 24 pH- Dependence of log k_A for the reaction of 4-chlorobenzenediazonium cation with sodium 2,3-dihydroxynaphthalene-6-sulphonate in borax (⊙) and borax-free (●) buffer



3.2.3. The effect of borax on the coupling reaction

It is known that borax forms complexes with certain aromatic diols [183] and in view of the suggested addition to 'diazo-coupler' formulations [58] it was decided to investigate any effect of complexation on the coupling reaction. This was accomplished by the following measurements. (i) The rate constant of coupling sodium 2,3-dihydroxynaphthalene-6-sulphonate to 4-chlorobenzenediazonium cations in a selection of buffers, including borax itself. (ii) The final visible spectra of the azo dyes from these reactions and also those resulting from the same arenediazonium cation with a selection of other couplers were compared in borax and phosphate buffers. (iii) Analysis of the azo dye products by paper and column chromatography. (i) - (iii) are described in more detail below.

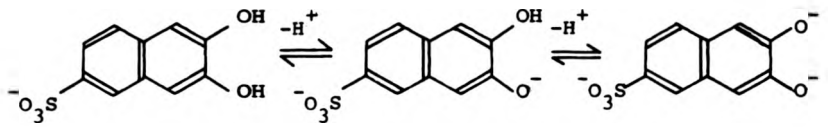
(i) The apparent second-order rate constants (k_A) between (XXX) and 4-chlorobenzenediazonium cations in solutions of different buffers in a pH range between 3 and 12 are displayed graphically in Fig. 24. The coupling reactions in borax and borax-free buffers have different rate constants because of the equilibrium between the coupler and its borate complex, viz.



(96)

Considering the coupling reaction in the borax-free buffers first, the plot of log k_A against pH (Fig. 24) consists basically of four regions. At pH values up to the pH equivalent to pK_{A1} of the coupler (pK_{A1} = 8.24), the concentration of the singly ionised naphtholate(XXXb) should increase 10-fold per unit rise in pH as

demonstrated by Putter [71] and others [59]. As a result, the theoretical

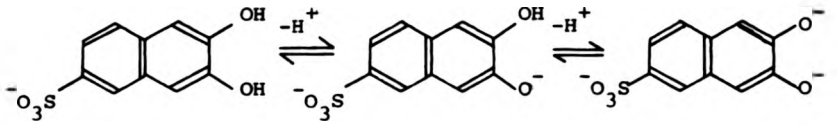


(97)

(XXXa) (XXXb) (XXXc)

gradient of the plot of the log k_A versus pH (below pH 8) is unity; however, the calculated value is somewhat less, i.e. 0.85, S.D = 0.08 with an absolute rate constant k = 1.48 x 10^4 $dm^3 mol^{-1} s^{-1}$. The reason for the low value of the gradient is unclear, but couplers having more than one activating group are found to give similar plots with gradients as low as 0.62 [63]. The fractional values were found with compounds such as resorcinol and so the reason may possibly be that there is some interference between adjacent or proximate goups. Putter [71] demonstrated that at pH ≥ pK_{A1}, the increase in the coupling rate constant with rise in pH approaches a maximum value and levels off to give a plateau region. The coupler in this reaction has two hydroxyl groups and as a result there is no plateau region, but merely a small inflection at ca. pH 8.7. This is caused by the merging of the region below ca. pH 8.5 with the similar one in the pH range between ca. 8.8 - 10. In the latter region, the doubly-ionised species (XXXc) is present at a concentration which increases, theoretically, ten-fold per unit rise in pH up to pH 12.13 = pK_{A2}. However, a gradient was found of only 0.77, S.D. = 0.04 with an average absolute rate constant of 1.17 x 10^7 dm^3 mol^{-1} s^{-1}. This discrepancy may possibly be explained by the following: 4-chlorobenzenediazonium cations have a pH_m value of 11.12 [129] and so above ca. pH 11 the competing reaction of the arenediazonium cation with OH^- to give the aryldiazotate takes place with a second-order rate constant of k_1 = 2.6 x 10^4 dm^3 mol^{-1} s^{-1}

demonstrated by Putter [71] and others [59]. As a result, the theoretical



(97)

(XXXa) (XXXb) (XXXc)

gradient of the plot of the log k_A versus pH (below pH 8) is unity; however, the calculated value is somewhat less, i.e. 0.85, S.D = 0.08 with an absolute rate constant k = 1.48 x 10^4 $dm^3 mol^{-1} s^{-1}$. The reason for the low value of the gradient is unclear, but couplers having more than one activating group are found to give similar plots with gradients as low as 0.62 [63]. The fractional values were found with compounds such as resorcinol and so the reason may possibly be that there is some interference between adjacent or proximate goups. Putter [71] demonstrated that at pH ≥ pK_{A1}, the increase in the coupling rate constant with rise in pH approaches a maximum value and levels off to give a plateau region. The coupler in this reaction has two hydroxyl groups and as a result there is no plateau region, but merely a small inflection at ca. pH 8.7. This is caused by the merging of the region below ca. pH 8.5 with the similar one in the pH range between ca. 8.8 - 10. In the latter region, the doubly-ionised species (XXXc) is present at a concentration which increases, theoretically, ten-fold per unit rise in pH up to pH 12.13 = pK_{A2}. However, a gradient was found of only 0.77, S.D. = 0.04 with an average absolute rate constant of 1.17 x 10^7 dm^3 mol^{-1} s^{-1}. This discrepancy may possibly be explained by the following: 4-chlorobenzenediazonium cations have a pH_m value of 11.12 [129] and so above ca. pH 11 the competing reaction of the arenediazonium cation with OH^- to give the aryldiazotate takes place with a second-order rate constant of k_1 = 2.6 x 10^4 dm^3 mol^{-1} s^{-1}

[124]. This is reflected by a levelling-off in the plot above pH 10, and above pH = pK_{A2} (12.13) the formation of the aryldiazotate [68] reduces the apparent rate constant and the gradient at pH > 12 becomes negative. Also some inaccuracy intrudes in the region where log k_A > 5 as the rate of reaction is near the limit of the stopped-flow apparatus, the reaction having $t_{\frac{1}{2}} \sim 5$ ms.

The pH-dependence of the rate constant below pH 6 is the same for the reaction in borax and borax-free buffers, presumably as no borate-complex is present in this pH range. As pH is increased, there is a sudden drop in the rate constant at ca. pH 6.4 which reflects the presence of a certain amount of the unreactive borate-complex. Between pH 6 and 7, the formation of the unreactive complex from the reactive species (XXXb) is demonstrated by the continued drop in rate constant despite the increase of $[OH^-]$ with rise in pH.

Table 17 shows that the rate constants calculated from the increase in O.D. at 380 nm are often substantially less than the equivalent values calculated from the data measured at 470 nm. This may be because the azo dye produced in this reaction reacts relatively slowly with borax to form a dye-borate complex which absorbs at ca. 390 nm.

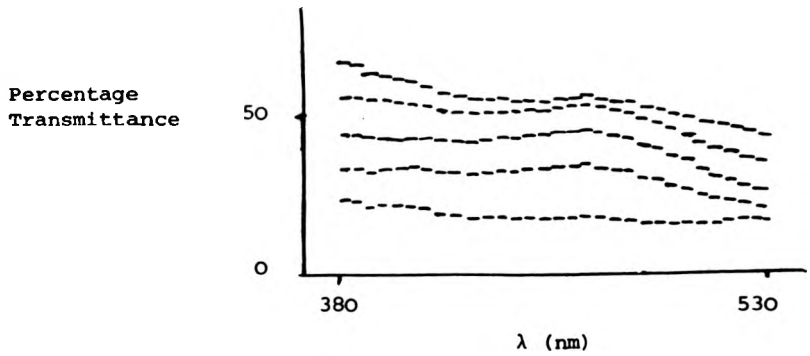
Table 17

Relative rate constants k_A calculated from data measured at 380 nm and 470 nm for the reaction of (XXX) with 4-chlorobenzenediazonium cations

pH	Apparent second-order rate constants k_A/dm^{3}mol^{-1}s^{-1}	
	380 nm	470 nm
9.17	147	164
9.54	420	547
10.07	1710	3270

The difference in the rates of reaction at 380 and 470 nm was also observed with the rapid scanning spectrometer, a typical series of spectra are given in Fig. 25.

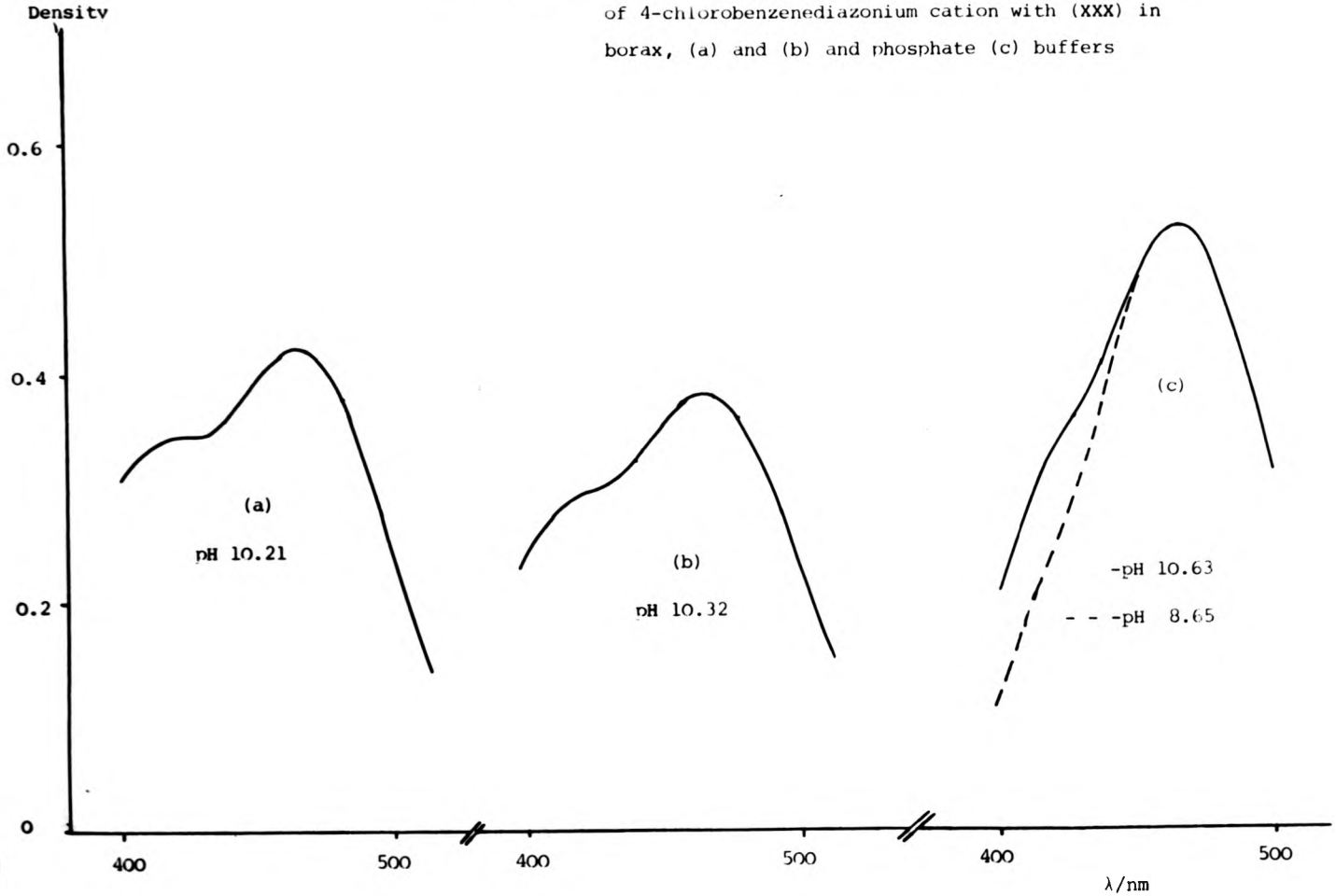
Figure 25 Series of spectra from the reaction of 4-chlorobenzenediazonium cation with XXX in a borax buffer.



The pH-dependence of log k_A at pH > 8 for the reaction performed in the borax buffer resembles the correlation obtained from the reaction in other buffers. We observe the plateau at ca. pH 8 - 9 probably caused by the same effect as that which produces the inflection in the borax-free buffered reaction profile. The gradient of the section of the borax-buffered pH-profile in the region pH 9 -11 is 1.49, S.D. = 0.07 which is greater than the theoretical value of unity expected if the ionisation of (XXXb) to (XXXc) were the sole factor causing an increase in rate constant with pH. The larger value may be explained by a shift in the equilibrium (96) towards the uncomplexed form of the coupler as $[OH^-]$increases. Presumably, at ca. 11, there is very little of the complex present because the rate constants obtained from the reactions in the borax and borax-free buffers coincide.

(ii) The visible spectra of the products from the reactions of 4-chlorobenzenediazonium cations and sodium 2,3-dihydroxynaphthalene-

Figure 26 Spectra from the azo dyes produced from the reaction of 4-chlorobenzenediazonium cation with (XXX) in borax, (a) and (b) and phosphate (c) buffers



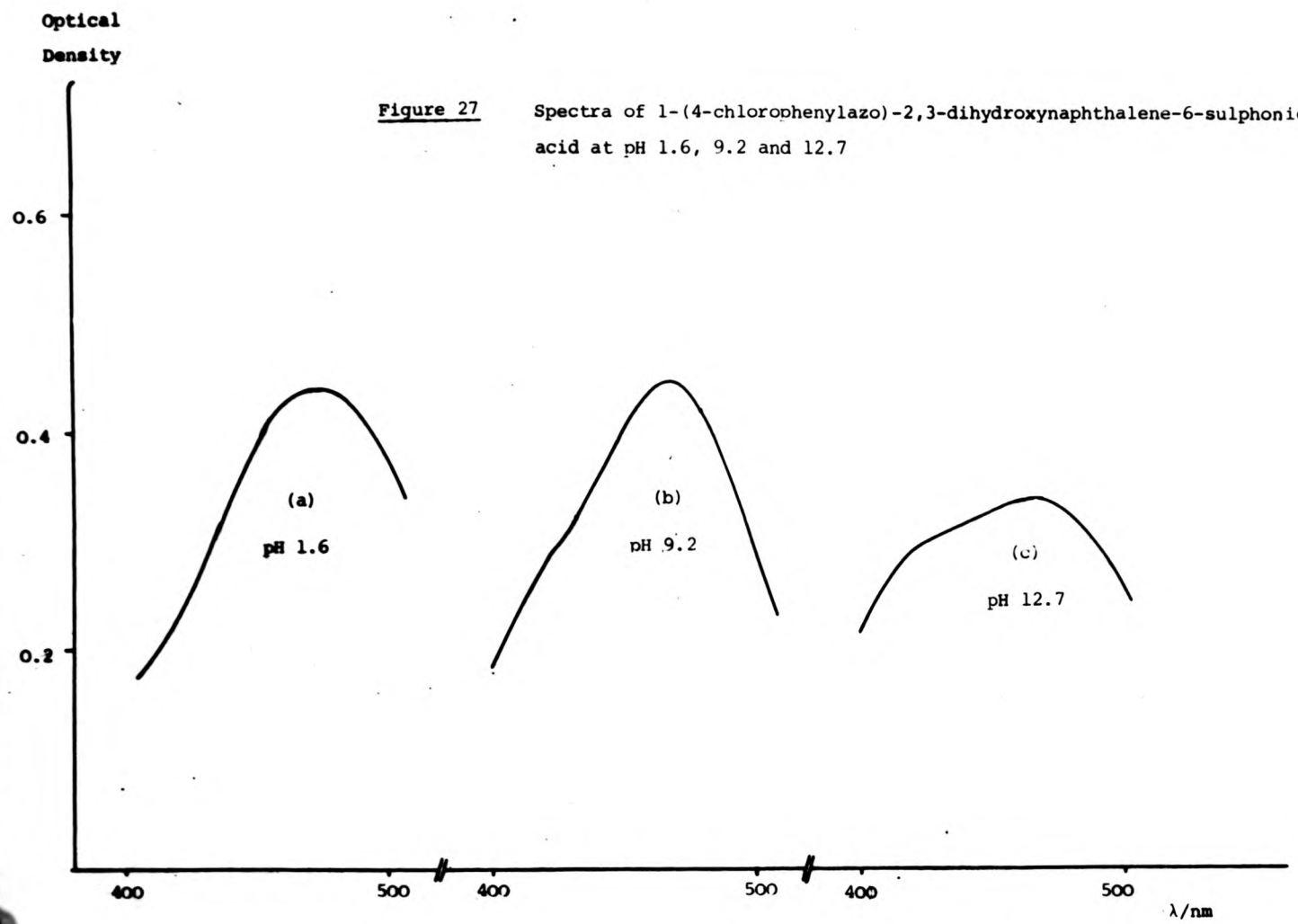


Figure 27 Spectra of 1-(4-chlorophenylazo)-2,3-dihydroxynaphthalene-6-sulphonic acid at pH 1.6, 9.2 and 12.7

-6-sulphonate (XXX) performed in five different types of buffer were recorded. The spectra of the four azo dye solutions prepared in phosphate, acetate, bicarbonate and 2-amino-2-(hydroxymethyl)-1,3-dihyroxypropane buffers are basically the same, small differences being attributable to the differences in their pH. Typical spectra of the azo dye solutions which were prepared in a phosphate buffer at pH values of 8.65 and 10.63 are given in Fig. 26 (c); they display λ_{max} 470 nm. The shoulder at low wavelength in the spectrum of the solution of higher pH may be due to the presence of a certain amount of the doubly-ionised form of the azo dye. If this is the case, then at a higher pH there will be more of the doubly-ionised form resulting in a corresponding difference in its visible spectrum. The spectrum of an azo dye solution, made at pH 12.7 (Fig. 27(c)) has λ_{max} 470 nm but with a lower extinction than the same solution prepared at pH 1.6 or 9.2 (Figs. 27(a) and (b)). The shoulder at ca. 400 nm which is attributed to the doubly-ionised form of the azo dye is much larger at pH 12.7 than at lower pH values.

The azo dye, 1-(4-chlorophenylazo)-2,3-dihydroxynaphthalene-6-sulphonic acid, prepared as described in section 2.1.13, was then dissolved in (0.02 M) hydrochloric acid and then diluted to yield a solution with a spectrum having a convenient optical density which is given in Fig. 27 (a). The pH was then adjusted to pH 9.22 by the addition of solid $NaHCO_3$ (Fig. 27(b)) and then further raised to a value of 12.7 by the addition of a few drops of 5 M NaOH (Fig. 27(c)). Adjustment of the pH of this solution to a very low value (ca. 1.0) with just sufficient concentrated HCl gave a spectrum almost identical to Fig. 27 (a), which suggests that the spectral changes are due solely to the reversible ionisation of the two hydroxyl groups.

The spectrum of this azo dye prepared in borax buffers exhibit an

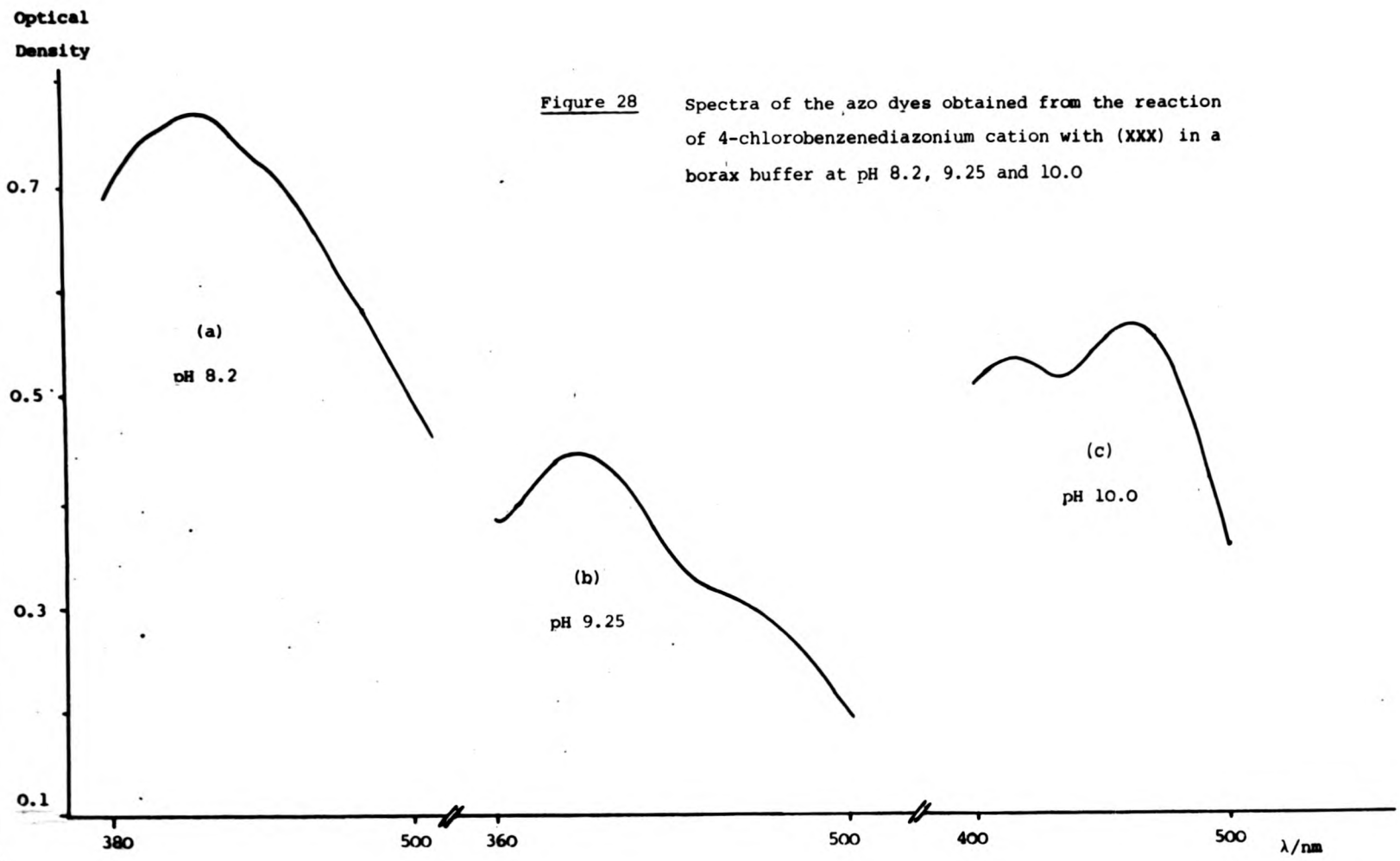


Figure 28 Spectra of the azo dyes obtained from the reaction of 4-chlorobenzenediazonium cation with (XXX) in a borax buffer at pH 8.2, 9.25 and 10.0

Figure 29

Spectrum of the solution obtained from 1-(4-chlorophenylazo)-2,3-dihydroxynaphthalene-6-sulphonic acid with a large excess of borax

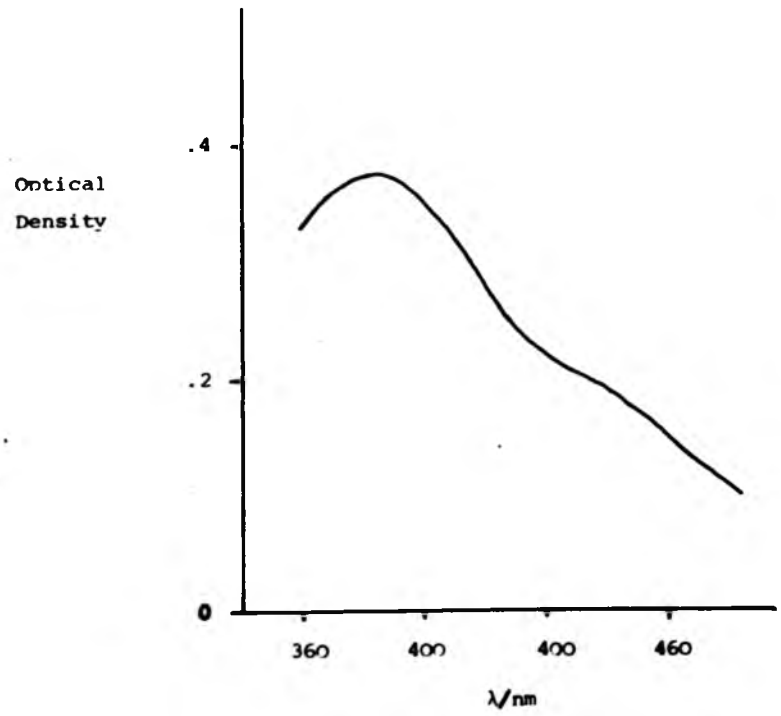
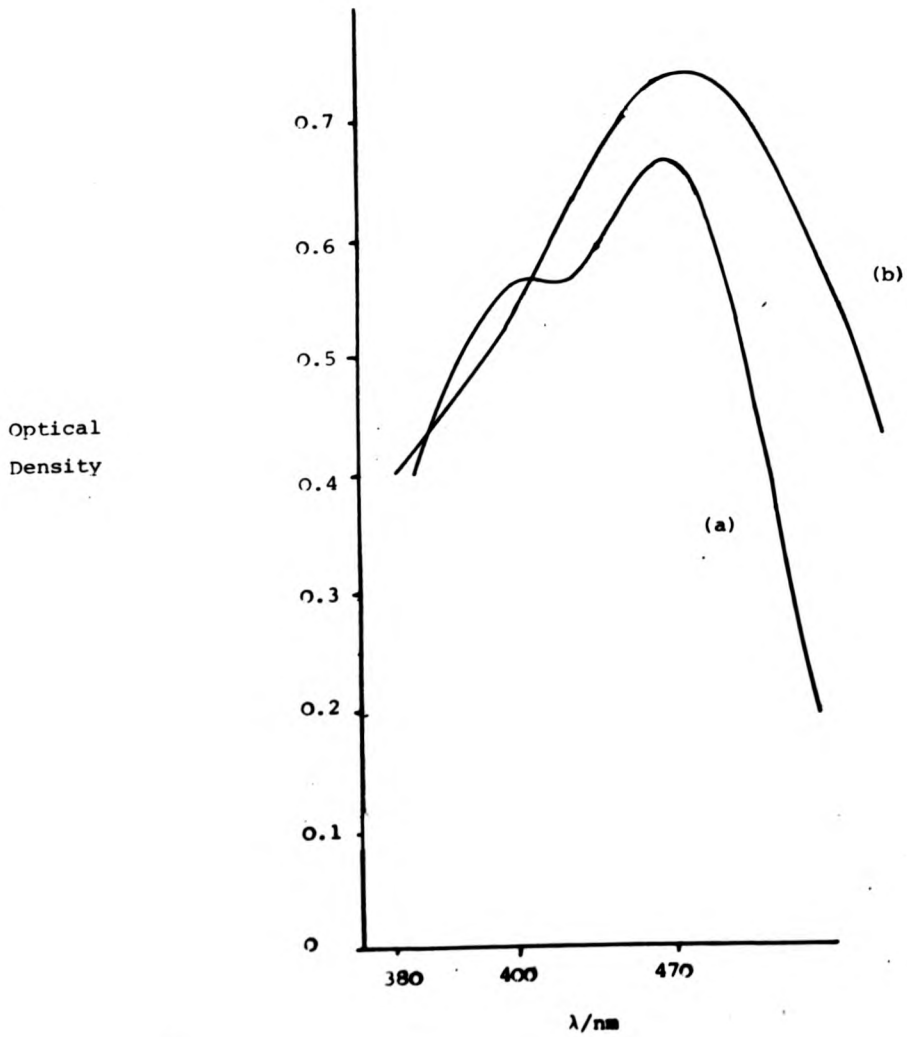


Figure 30

Spectra of 1-(4-chlorophenylazo)-2,3-dihydroxynaphthalene-6-sulphonic acid prepared in a borax buffer (a) and then acidified to obtain (b)



absorption at ca. 400 nm (see Figs. 26(a), (b), 28(a) - (c)). This is unlikely to be the doubly-ionised form of the azo dye as this is observed only at much higher pH (cf. Fig. 27). The species which absorbs at ca. 400 nm is therefore probably the borate complex of the azo dye. The uncomplexed and complexed forms of the dye are produced in the pH range between pH 6 - 11 and the ratio [free azo dye]/[complexed dye] increases with increase in pH. The two forms of the azo dye have different λ_{max} :

Uncomplexed form, λ_{max} = 470 nm

Borate-complex, λ_{max} = ca. 390 nm

The change in the relative proportions of the two components is illustrated by the spectra of their solutions at various pH values. cf. Fig. 26(a), (b) and Fig. 28 (a) - (c). At the lowest value of pH chosen (pH 8.2), the borate-complex azo dye predominates but as the pH increases, the proportion of the uncomplexed form increases until at pH $\geq$ 11 there is no difference between the spectra of the azo dye prepared in borax and borax-free buffers. The addition of an excess of borax to a solution of the azo dye produced in a phosphate buffer gives a solution with the spectrum shown in Fig. 29, which is similar to that in Fig. 28(a), indicating that the form of the azo dye which has λ_{max} = 390 nm is a complex between borax and the azo dye. The instability of the complex in acidic media was demonstrated by the addition of acid (1M HCl) to a solution of the azo dye produced in a borax buffer at pH ca. 10. (Fig. 30), which resulted in a solution with a spectrum almost identical to that in Fig. 27(a).

In order to ascertain the requirements for the formation of coupler-borate and azo dye-borate complexes, the azo dyes from

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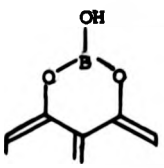
In order to ascertain the requirements for the formation of coupler-borate and azo dye-borate complexes, the azo dyes from

4-chlorobenzenediazonium cations with seven hydroxynaphthalene couplers were prepared in (a) phosphate and (b) borax buffers (at ca. pH 9.6) and the visible spectra of the resulting azo dyes compared.

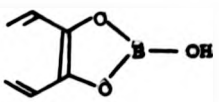
The following couplers were used in this study:

2,3-dihydroxynaphthalene-6-sulphonic acid	(XXX)
2,3-dihydroxynaphthalene	(XXIX)
1,8-dihydroxynaphthalene-3,6-disulphonic acid	(XXXIV)
2,7-dihydroxynaphthalene-3,6-disulphonic acid	(XXXII)
2,7-dihydroxynaphthalene	(XXXI)
1,5-dihydroxynaphthalene	-
2-naphthol-6-sulphonic acid	(XXVII)

The azo dyes obtained from (XXX), (XXIX) and (XXXIV) had markedly different spectra in borax as compared to phosphate buffers, whereas the remaining couplers from the above list gave azo dyes with spectra which were almost the same in both types of buffer. The behaviour of the azo dye from (XXIX) and the 4-chlorobenzenediazonium cation is identical to that from (XXX) with the same arenediazonium ion, which has been described above. The similar azo dye from (XXXIV) as the coupler gave a mauve solution in a phosphate buffer with λ_{max} 500 nm whereas in a borax buffer, an orange solution with a single absorption, λ_{max} = 470 nm was observed. The critical feature showed by (XXX), (XXIX) and (XXXIV) which differentiates them from the other couplers is the proximity of their hydroxyl groups. When these are in the 2,3- or 1,8- positions they are capable of forming rings with the boron atom of borax, thus:



(XXXIX)



(XL)

The coupling of arenediazonium cations to (XXXI) in a borax buffer of pH 9.6 gives predominantly the borate-complex (XXXIX) of the azo dye whereas under the same conditions, both (XXX) and (XXXIX) yield a mixture containing < 50% of the complexed azo dyes. The difference is probably due to the greater stability of the non-planar six-membered ring in (XXXIX) than the distorted five-membered ring in (XL).

(iii) Samples were prepared of the azo dye (or dyes) from the reaction of 4-chlorobenzenediazonium cations with excess of (XXX) as described in section 2.1.13, with and without the presence of borax or other buffers, as were also two samples with excess of the arenediazonium salt. The six azo dye products, together with the conditions of their preparation, the number of components and their R_f values, obtained by paper chromatography with 20% aqueous methanol as the solvent, are given in Table 18.

Table 18

R_f values of separated components from the product of the reaction between 4-chlorobenzenediazonium cations and (XXX)

Reactant in Excess	Buffer Present	Number of separated components	R_f values
Coupler	none	2	0.38,0.78
Arenediazonium salt	"	2	0.017,0.38
"	borax	2	0.034,0.38
Coupler	"	3	0.38,0.68,0.78
"	phosphate	2	0.38,0.78
"	acetate	2	0.38,0.78

(N.B. The R_f values in Table 18 are averages from a number of chromatograms).

These results indicate that only one azo dye is produced from the reactions with excess coupler in the absence of borax; however, in a borax buffer, two azo dyes are obtained. Some of the bis-azo dye is also formed in the reactions with an excess of the arenediazonium cation. The component with an R_f value of 0.78 is remaining coupler from the reaction where it was added in excess, which could only be observed either after it had oxidised by aerial oxidation or 'developed' with an arenediazonium salt solution. The components are listed with their R_f values in Table 19.

Table 19

R_f values of the components from the coupling reaction between (XXX) and 4-chlorobenzenediazonium cations

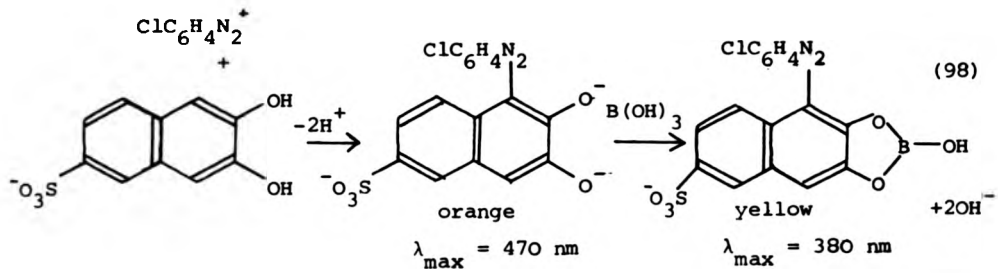
Component	Colour	R_f value
Mono-azo dye without borax	orange	0.38
Mono-azo dye with borax	orange	0.38
"	yellow	0.68
Bis-azo dye without borax	mauve	0.017
Bis-azo dye with borax	mauve	0.038
(XXX)	colourless–pale yellow	0.78

The individual components from the products of the above reaction were isolated by column chromatography using an alumina column with 50% aqueous methanol as eluent. The results were as follows:

(i) From the reaction with an excess of coupler in a phosphate buffer, one orange dye was separated with λ_{max} = 470 nm.

(ii) The reaction with excess coupler in a borax buffer yielded two azo dyes, one yellow with λ_{max} = 380 nm and

the other orange with λ_{max} = 470 nm. The spectrum of the second dye was very similar to that of the azo dye extracted from the products of the reaction performed in a phosphate buffer. The yellow dye, on acidification, was transformed to an orange dye with λ_{max} = 470 nm, presumably identical to the other azo dye products with the same λ_{max}. If the yellow dye is the azo dye-borate complex and the orange dye is the uncomplexed dye, then the reaction is:



(98)

(iii) From an excess of the arenediazonium cation in a phosphate buffer, one dye was obtained with λ_{max} = 400 nm.

(iv) The product from the reaction with an excess of arenediazonium cation in a borax buffer could not be separated completely, but there appeared to be three azo dyes, one being the mono-azo dye and the other two the complexed and uncomplexed bis-azo dyes with λ_{max} = 370 nm and ca. 400 nm respectively.

Finally an attempt was made to discover the extent of complex formation from (XXX) and borax.

Method

The following solutions were prepared and their absorbance at 322 nm and λ_{max} recorded (Table 20). Aqueous borax (0.025 M) was

added to a solution of 0.001 M (XXX) and the pH readjusted with dil. HCl (0.1 M) to ca. 5.6. This solution was then made up to 25 cm^3 with buffer so as to keep the pH and coupler concentration constant.

Table 20

Optical density and λ_{max} of the product from (XXX) with borax

pH	Vol. of aq. $Na_2B_4O_7$ (cm^3) added to (XXX) (5 cm^3)	O.D. (332 nm)	λ_{max} nm
5.65	0	0.44	315
5.65	2	0.46	316
5.68	5	0.505	317
5.68	10	0.575	318

The results from Table 20 indicate that the equilibrium (96) depends on [borax] and the equilibrium constant K is probably substantially less than one

$$K = \frac{[\text{borate complex}]}{[\text{coupler}]\,[\text{borax}]} < 1 \qquad (99)$$

3.3 The aromatic diazonium cation-diazotate equilibrium

The apparent rate constant of certain reactions between arenediazonium cations and couplers at high pH are known to reach maxima [68] for example in the coupling of sodium 2,3-dihydroxy-naphthalene-6-sulphonate (XXX) and sodium 2-naphthol-6-sulphonate (XXVII) with 4-chloro and 4-methylbenzenediazonium cations as illustrated in Table 21.

Table 21

pH - dependence of the apparent rate constant (k_A) of the coupling between 4-methylbenzenediazonium cation and (XXX)

pH	k_A ($dm^3 mol^{-1} s^{-1}$)
11.33	6.35×10^4
11.89	1.12×10^5
11.94	2.89×10^4
12.65	1.07×10^4
12.90	3.36×10^3

The rate maxima are explained [68] by the formation of aryldiazotates as described in section 1.4. In our study of these equilibria, the reactions have been divided up into four categories, viz.

(i) the reactions of syn-aryldiazotate with H^+

(ii) the reactions of anti-aryldiazotate with H^+

(iii) the formation of syn-aryldiazotates from the reaction of arenediazonium cations with base.

(iv) the isomerisation of syn-aryldiazotates to the corresponding anti-form.

3.3.1 The reaction of syn-aryldiazotates with H^+

Syn-aryldiazotates with no strongly electron-withdrawing substituents in the 2- and 4- ring positions are relatively stable and their reactions may be followed by conventional spectroscopic techniques, whereas compounds having such groups rapidly isomerise to the corresponding anti-form which illustrates the use of the quenched stopped-flow apparatus. The 4-chloro compound was chosen as an example of a stable syn-aryldiazotate which was conveniently prepared by the addition of a few cm^3 of a slightly acidic solution

of the corresponding arenediazonium cation to 0.25 M NaOH. Its reactions at ca. pH 13 were followed after the addition of one of a selection of five couplers in buffered solution.

With each of the five couplers, the dependence of the rate constant (for appearance of dye) on the coupler concentration was determined, and with 2-naphthol the dependence on pH was also investigated. At ca. pH 13, the two fastest couplers, 2,3-dihydroxynaphthalene and its 6-sulphonic acid analogue are present in the form of their doubly-ionised species. The rate constant of the reaction between 4-chlorobenzenediazonium cations and the latter (XXXc) is 1.45×10^4 $dm^3 mol^{-1} s^{-1}$. The rate constant for the dye formation from the corresponding syn-aryldiazotate at pH 12.8 is independent of the coupler concentration and also is the same, within experimental error, for both couplers with a value of 0.26 s^{-1}. (This value is the average from a number of experiments, all results lying within 5% of the quoted figure, and reactions obeying first order kinetics.) These results are consistent with the rate-determining step of this reaction being the conversion of the syn-aryldiazohydroxide to the arenediazonium salt, (eqn. 44).

Sterba et al [124] have measured the rate constants of the reactions of a series of syn-aryldiazotates with acid at pH values below pH 7.5 where the rate determining step is the splitting of the N - O bond in the aryldiazohydroxide, the concentration of which is pH-dependent (see section 1.4.2). The rate constants k_{-1} is related to the apparent rate constant k_A by eqn. (100).

$$k_A = k_{-1} ([H^+]/([H^+] + K_2)) \qquad (100)$$

The equilibrium constants K_2 were found from plots of log k_A versus pH; however, this was not possible with the reactions of syn-4-chlorobenzenediazotate as at ca. pH 7, the reaction is too

of the corresponding arenediazonium cation to 0.25 M NaOH. Its reactions at ca. pH 13 were followed after the addition of one of a selection of five couplers in buffered solution.

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$$k_A = k_{-1} ([H^+]/([H^+] + K_2)) \qquad (100)$$

The equilibrium constants K_2 were found from plots of log k_A versus pH; however, this was not possible with the reactions of syn-4-chlorobenzenediazotate as at ca. pH 7, the reaction is too

fast to follow. K_2 for this component was therefore found by extrapolation of a Hammett plot of Sterba's values of K_2 against the corresponding σ-constants and was found to be 2.0×10^{-8} (i.e. $pK_2 = 7.70$). Inserting this value for K_2 into eqn. (100) yields a rate constant (k_{-1}) of 3.20×10^4 s^{-1}.

With 2-naphthol as the coupler the apparent rate constant of the dye formation was found to be dependent on both the coupler concentration and the pH of the solution. This compound couples relatively slowly compared to the two previous examples and these two concentration dependences indicate that the coupling reaction is the rate determining step of (101)

$$\underline{\text{syn}}\text{-ClArN}_2\text{O}^- \xrightarrow{+H^+} \underline{\text{syn}}\text{-ClArN}_2\text{OH} \xrightarrow{-OH^-} \text{ClArN}_2^+ \xrightarrow[\text{slow}]{+\text{2-naphthol}} \text{azo dye} \quad (101)$$

If the rate determining step is the coupling reaction,

then $$\frac{d[\text{azo dye}]}{dt} = k\,[ArN_2^+][C] \quad (102)$$

where $[ArN_2^+]$ is the arenediazonium salt concentration,

[C] is the concentration of the coupler,

and k is the coupling rate constant.

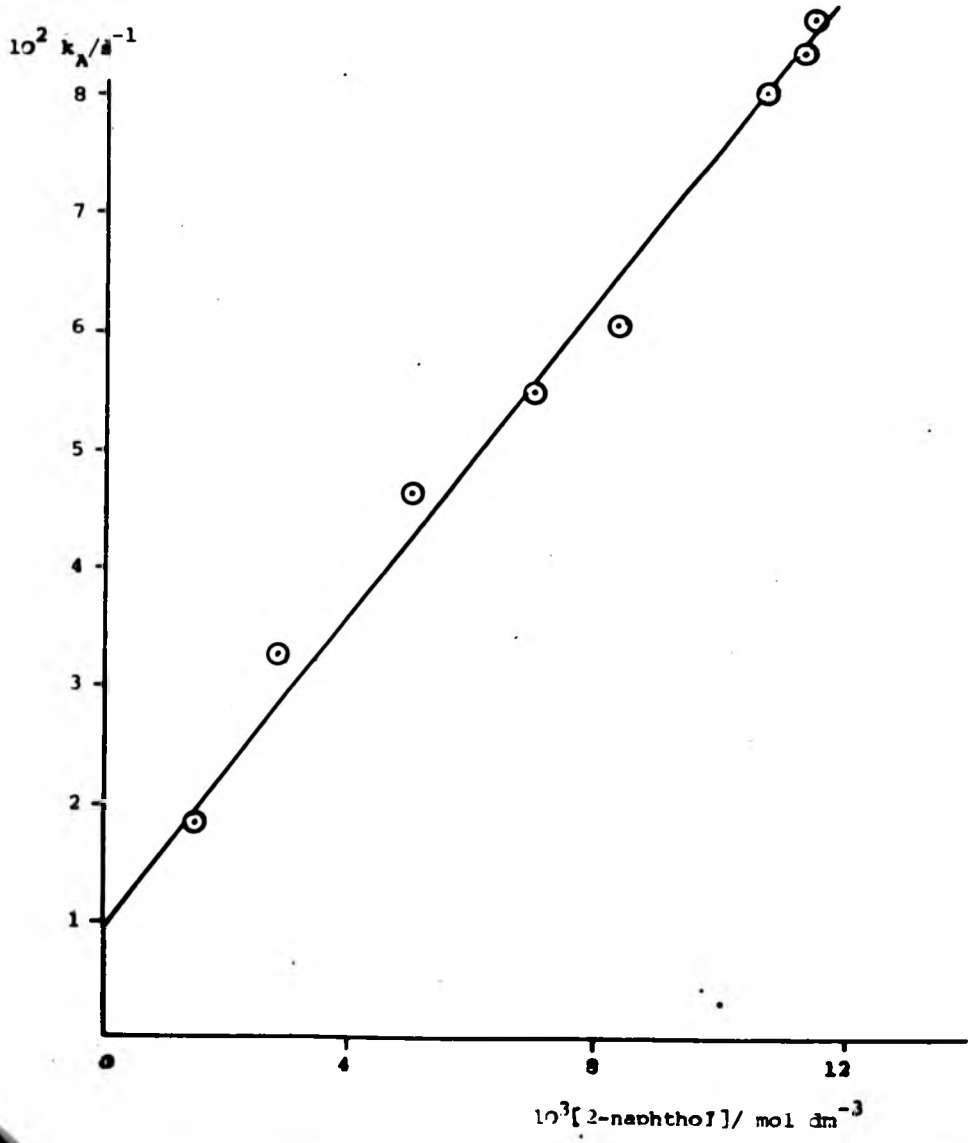
Now $[ArN_2^+]$ is unknown, but it can be related to the syn-aryldiazotate concentration from (44) and (45) (section 1.4.2), viz.

$$K_1 = \frac{[\underline{\text{syn}}\text{-}ArN_2OH]}{[ArN_2^+][OH^-]} \quad (44)$$

$$K_2 = \frac{[\underline{\text{syn}}\text{-}ArN_2O^-][H^+]}{[ArN_2OH]} \quad (45)$$

$$\text{which gives } K_1K_2 = \frac{[\underline{\text{syn}}\text{-}ArN_2O^-][H^+]}{[ArN_2^+][OH^-]}$$

Figure 31 Plot of the apparent rate constant (k_A) against coupler concentration for the reaction between syn-4-chlorobenzenediazotate at pH 13.04



(k_A) against
ion between
3.04

Figure 32 Dependence of apparent first-order rate constant for dye formation on [coupler] for the reaction: syn-4-chlorobenzenediazotate + 2-naphthol at pH 12.23

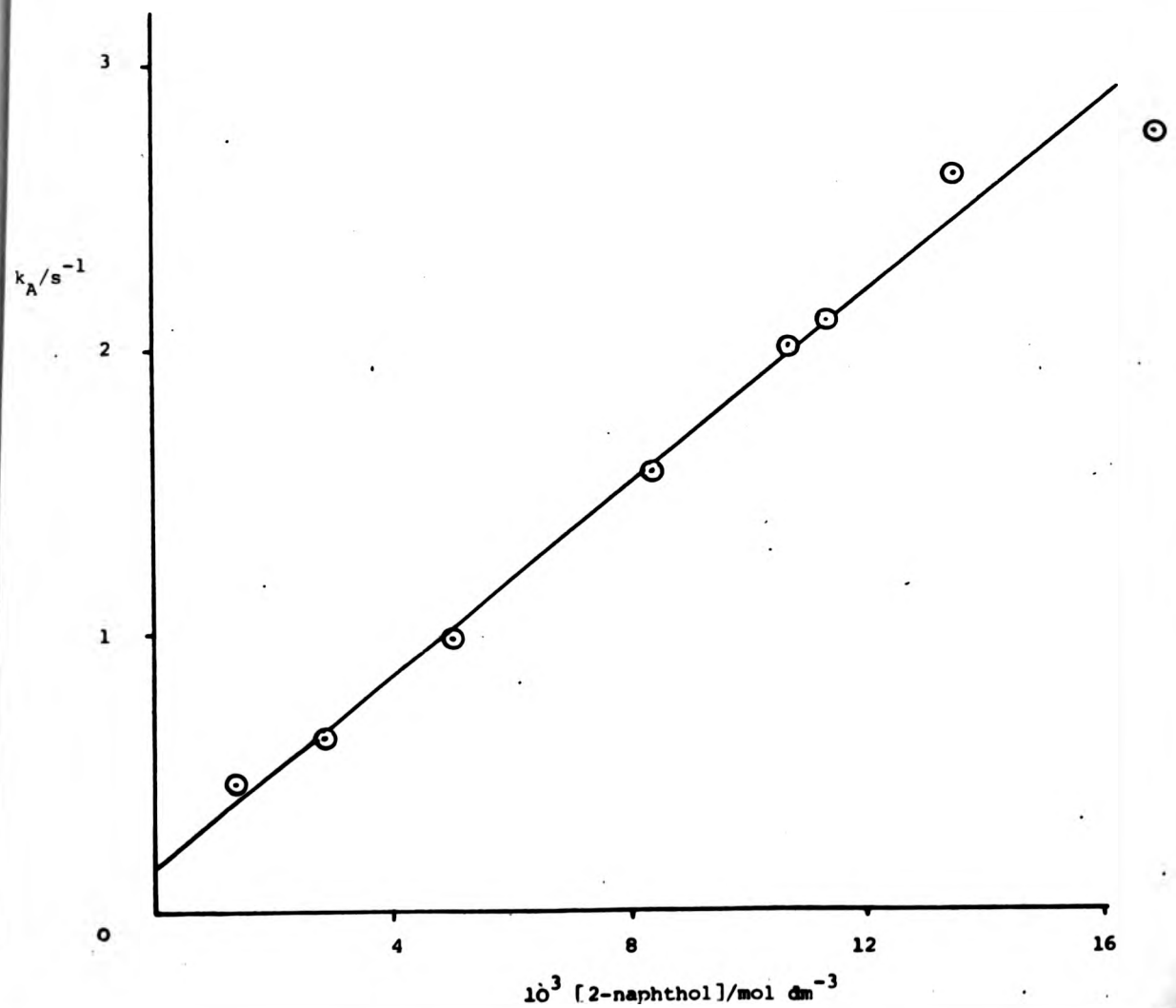
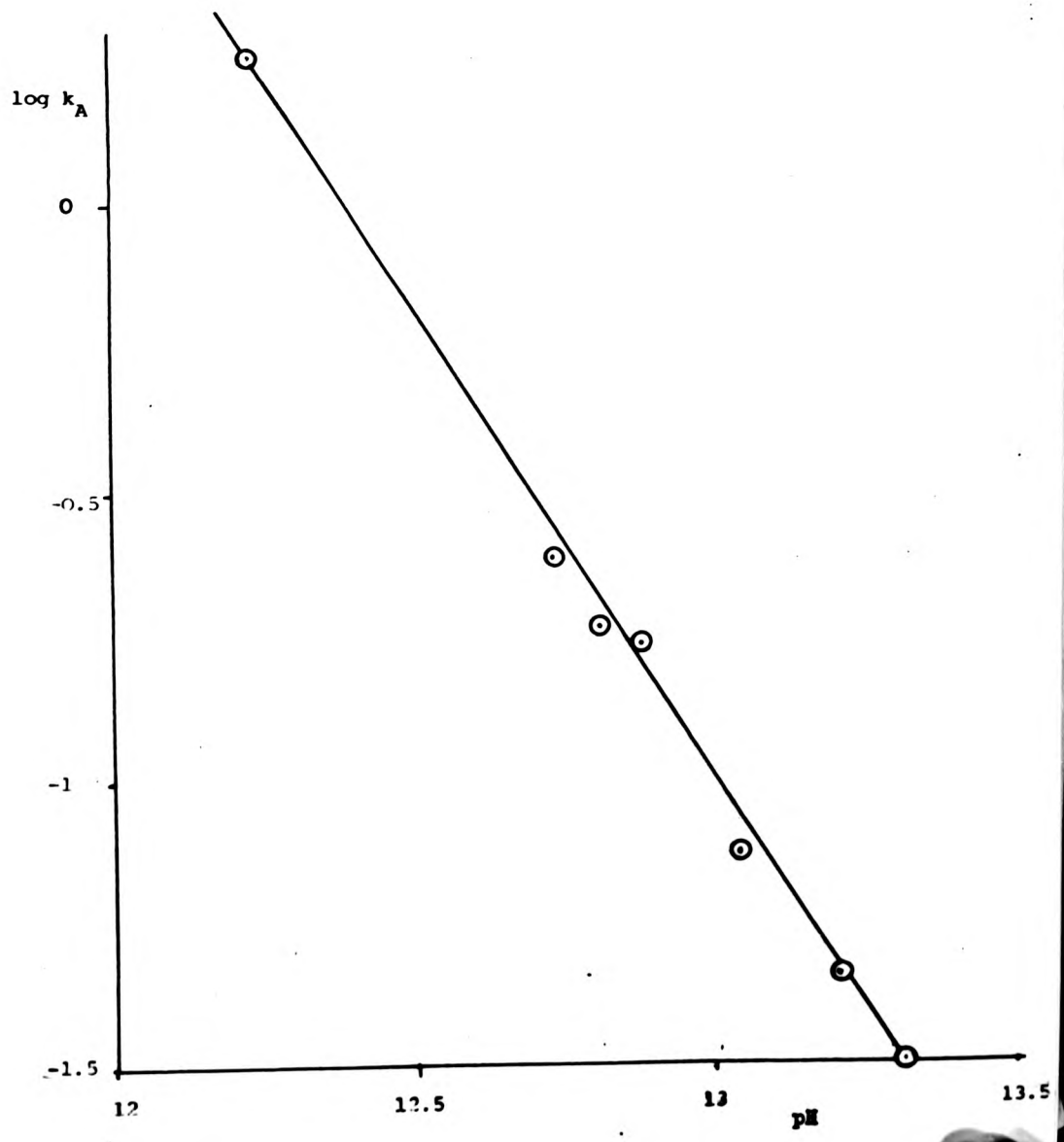


Figure 33

pH- Dependence of the apparent rate constant for the reaction of syn-4-chlorobenzenediazotate with 0.01 M 2-naphthol



and hence:

$$[ArN_2^+] = [\underline{syn}\text{-}ArN_2O^-] \; Kw/K_1K_2 \; [OH^-]^2 \qquad (103)$$

where $K_w = 10^{-14}$

(103) may be combined with (102) to yield (104)

$$\frac{d[\text{azo dye}]}{dt} = \frac{k\,K_w[\underline{syn}\text{-}ArN_2O^-][C]}{K_1K_2\,[OH^-]^2} \qquad (104)$$

and hence the rate of reaction should be linearly proportional to the concentration of coupler and inversly proportional to $[OH^-]^2$.

Two examples of the dependencies of the apparent rate constant k_A on the concentration of 2-naphthol are given in Figs. 31 and 32. These plots, together with several determined at other pH values are linear, although they do not pass through the origin (the intercept depending on pH). This suggests that there may be a simultaneous reaction occurring which is also pH-dependent. One possible alternative reaction pathway is the thermal decomposition of the arenediazonium cation, but it is unclear as to how this produces the observed kinetic behaviour. Further evidence for the occurrence of a competing reaction was obtained from the dependence of k_A on pH, which has a gradient of only -1.62, somewhat less than the theoretical value of -2.0 from (104), (Fig. 33).

The result obtained from the reactions of the less reactive coupling compounds, 2-naphthol-6-sulphonic and 6,8-disulphonic acids with <u>syn</u>-4-chlorobenzenediazotate gave only approximate first order behaviour indicating that either the reaction is not strictly first-order or, more probably, that more than one reaction is involved. Two further observations from the reactions with the former coupler which indicate the presence of a competing reaction

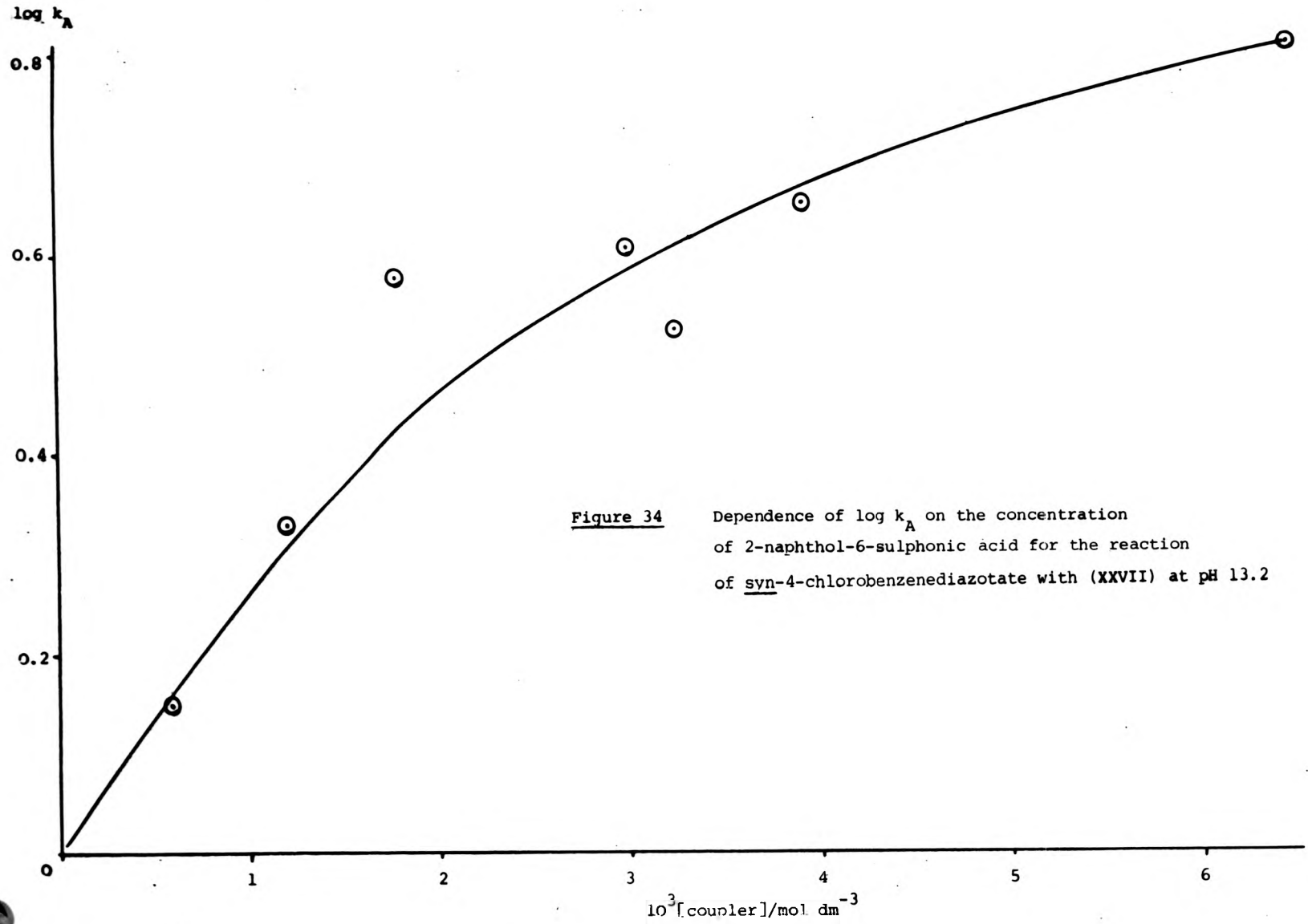


Figure 34 Dependence of log k_A on the concentration of 2-naphthol-6-sulphonic acid for the reaction of syn-4-chlorobenzenediazotate with (XXVII) at pH 13.2

pathway are:

(i) the graph of log k_A against coupler concentration at pH 13.2 (Fig. 34) is not linear, although the points are widely scattered.

(ii) the final optical density of the solutions of the resulting azo dye increases regularly with the coupler concentration. Those observations indicate a larger contribution from the simultaneous competing reaction than when 2-naphthol is employed as the coupler. With 2- naphtol-6,8-disulphonic acid as the coupler, no azo dye is produced, but only phenolic compounds, probably decomposition products of the intermediate arenediazonium ions. The rate constants of the reactions in the presence of this coupler are independent of its concentration and are $k_A = 2.7 \times 10^{-3}\ s^{-1}$.

We conclude that the reactivity of the coupler determines the reaction pathway as follows: the reaction with 2,3-dihydroxynaphthalene and its -6-sulphonic acid analogue is probably (101), with the N–O bond splitting of the aryldiazohydroxide as the slowest step. With 2-naphthol, the rate-determining step is the coupling reaction, although there is some contribution from the decomposition of the arenediazonium cations. The thermolysis of ArN^+_2 becomes appreciable with 2-naphthol-6-sulphonic acid (both the coupling and thermolysis reactions proceeding at similar rates) and with the slowest coupler, 2-naphthol-6,8-disulphonic acid, it becomes the predominate fate of the intermediate 4-chlorobenzenediazonium ions.

The reaction with acid of aryldiazotates having strongly electron-withdrawing substituents was followed with the 'quenched stopped-flow' apparatus which is described in section 2.3.3. The reactions of the 2- and 4-nitro compounds were first monitored by the formation of the azo dye from the resulting arenediazonium

cations and sodium 2,3-dihydroxynaphthalene-6-sulphonate (added with the acid at the second mixing point). The apparent rate constants k_A were found to be as follows

(i) Reaction of 4-nitrobenzenediazotate with H_3O^+ and coupler

pH	$k_A(s^{-1})$
6.22	11.6
6.72	12.2
7.04	10.5

(ii) Reaction of 2-nitrobenzenediazotate with H_3O^+ and coupler at pH 6.74

[coupler]	$k_A(s^{-1})$
0.0015 M	6.5
0.0035 M	8.3
0.0070 M	11.8

The rate constant k_A of the reaction of the 2-nitro compound increases with coupler concentration although the gradient does not pass through the intercept but at $k_A = 5.0\ s^{-1}$. This suggests that the coupling rate constant is not very dissimilar to the rate constant k_{-1}. Calculation of the theoretical pseudo first-order rate constant for the coupling reaction under these conditions (from the absolute coupling rate constant given in section 3.2.1) yields a value of ca. 6 s^{-1} and so we conclude that the above values of k_A probably do not refer to the rate constants of the N-O bond splitting of the syn-aryldiazohydroxides. Unfortunately, the rate constants for the 2- and 4- nitro compounds could not be measured in the absence of coupler for two reasons:

(i) At pH < ca. 6, the reaction is too fast to be monitored with the apparatus in its present form, the reaction being complete within the mixing time of the instrument, which is prohibitively

long (ca. 0.2s) because of the lack of a stop-syringe (see section 2.3.3). It was estimated that with the 4-nitro component at pH ca. 6 that $t_{\frac{1}{2}} < 0.02s$, i.e. $k_A > 35s^{-1}$.

(ii) At higher pH the thermal decomposition of the arenediazonium salt becomes appreciable and prevents measurement of the rate constant k_A. Because of these problems different substituted aryldiazotates were chosen for this type of kinetic study. The wavelengths at which these reactions were observed were chosen by comparison of the spectra of the arenediazonium salts with those of the corresponding aryldiazotates, and a complete list of the wavelengths (λ) selected is given in Table 22.

Table 22

Wavelengths (λ) utilised for the observation of the reaction of syn-aryldiazotates with H_3O^+

Substituted	λ(nm)
2-NO_2	310
4-NO_2	260
3-NO_2	233
2-Cℓ-4-NO_2	265
2-NO_2-4-Cℓ	310

At the monitoring wavelengths given in Table 22, the formation of the corresponding arenediazonium salt was recorded by the increase in its optical density. It was discovered that above a certain pH (different for each compound), the rate of decomposition of the arenediazonium salt became appreciable and as a result the rate constants could not be measured accurately. Due to the long mixing-time of the apparatus, as the pH of the reaction medium is

progessively reduced, there reaches a point where the rate becomes too fast to obtain accurate rate data and as a result, reasonably accurate rate constants were measured only within a fairly small range of pH, e.g. the 2-Cl-4-NO_2 compound was examined in the pH range 4.6 - 6.7.

It was found to be impossible to ascertain whether this method gives rate constants similar to those which have been previously measured by alternative methods. This is because most of the present known literature values refer to rate data for the reaction of compounds which react too quickly with H_3O^+ to be followed with this apparatus.

The most accurate results were obtained from the reactions of the 2-nitro-4-chloro- and 2-chloro-4-nitro compounds, the rate constants for which are given in Table 23.

Table 23

Rate constants for the reactions of syn-aryldiazotates with H_3O^+

Aryldiazotate ring substituents	pH	$k_A(s^{-1})$
2-Chloro-4-nitro	4.62	9.0
	5.17	12.5
	5.93	2.45
	6.21	1.55
	6.35	1.15
	6.71	1.03
2-Nitro-4-chloro	4.62	11.1
	5.17	8.9
	6.16	4.61
	6.35	2.60
	6.70	1.82
	7.16	0.59

Figure 35 pH-Dependence of log k_A for the reaction of 2-nitro-4-chloro (⊗) and 2-chloro-4-nitrobenzenediazotate (⊙) with acid

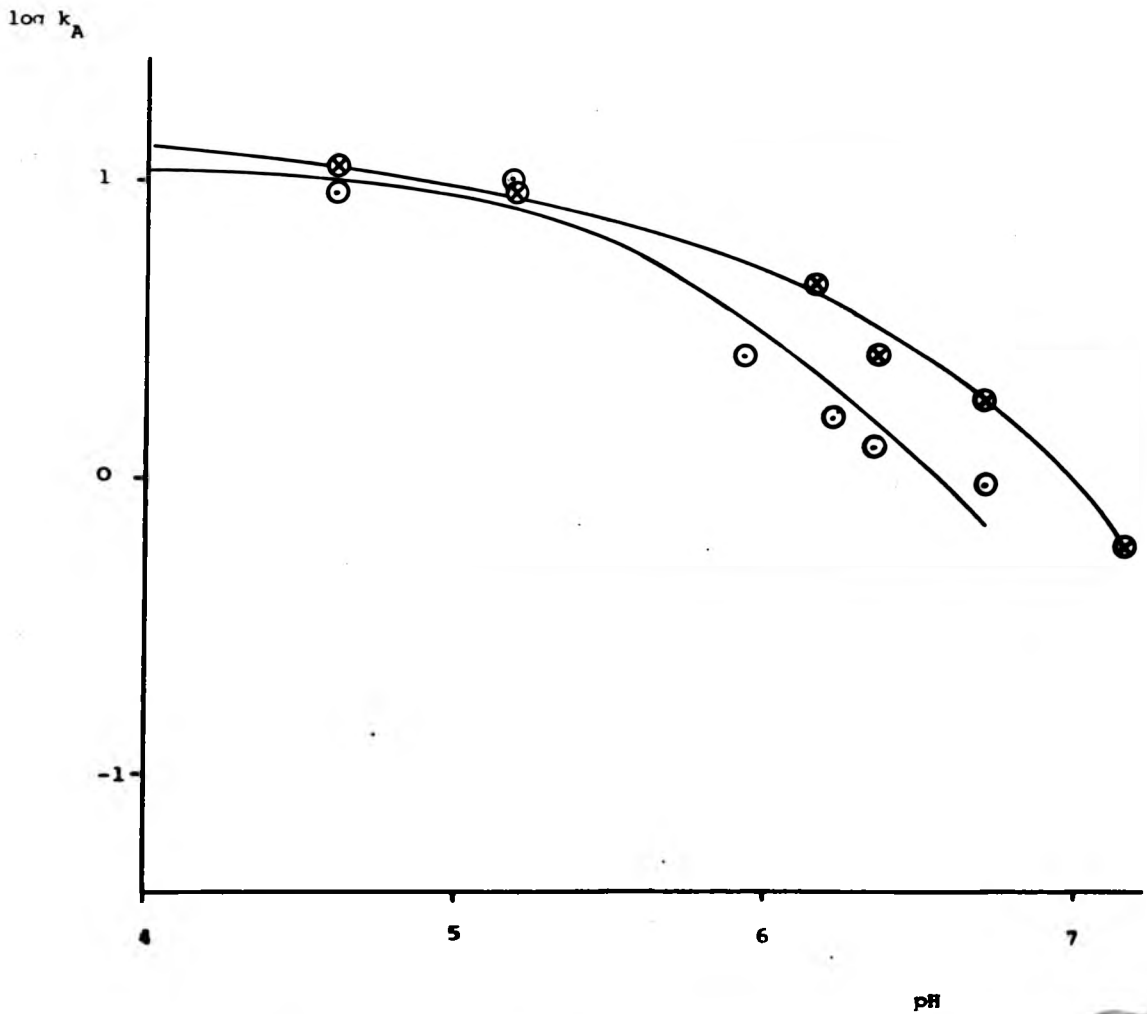
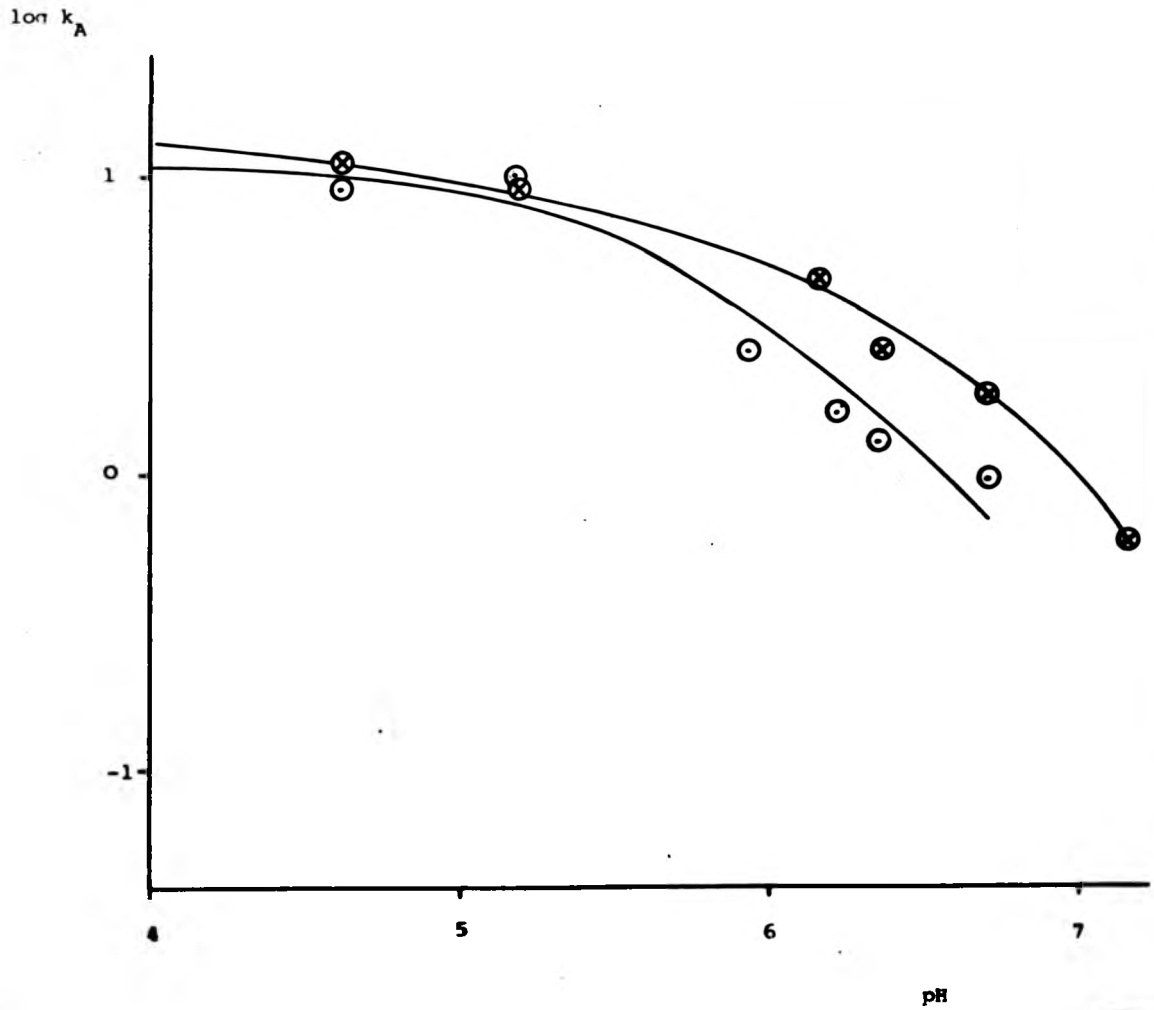


Figure 35 pH-Dependence of log k_A for the reaction of 2-nitro-4-chloro (⊗) and 2-chloro-4-nitrobenzenediazotate (⊙) with acid



The dependences of log k_A on pH for the reactions of the two aryldiazotates in Table 23 are given in Fig. 35. There appears to be a plateau region in the plot for the 2-chloro-4-nitro compound at pH < 5.2 with k_A = ca. $10s^{-1}$. The plot from the 2-nitro-4-chlorobenzenediazotate ions gives a reasonably smooth curve which levels off below the lowest pH value which could be utilised. The plateau is estimated to be at ca. $k_A = 16s^{-1}$. The plots given in Fig. 35 are comparable to the range pH5 - 7 in Fig. 3(b); which refers to the similar reaction of the 3-nitro-4-chloro compound [121]. On addition of acid to the syn-aryldiazotate, a certain amount of the syn-aryldiazohydroxide is produced almost immediately and the N-O bond splitting of this intermediate in the rate-determining step. The true rate constant k_{-1} is related [124] to k_A by eqn. (100).

$$k_A = k_{-1}[ArN_2OH]/([ArN_2OH]+[ArN_2O^-]) = k_{-1}([H^+]/([H^+] + K_2)) \quad (100)$$

In the plateau region, all of the syn-aryldiazotate is converted to the corresponding syn-aryldiazohydroxide and therefore $k_A = k_{-1}$. From Fig. 35 the values of k_{-1} are ca. $10s^{-1}$ and ca. $16s^{-1}$ for the reaction of the 2-chloro-4-nitro and the 2-nitro-4-chlorobenzenediazotates respectively. Unfortunately there is insufficient data to determine the equilibrium constants K_2 from these plots, however, K_2 may be calculated from equation (100) using our values of k_{-1} and the rate constants k_A in the pH range above the plateau region. (Calculation of K_2 from values in the plateau region gives negative values). The calculated values of pK_2 are summarised in Table 24.

Table 24

Calculated values of pK_2 from the reaction of

syn-aryldiazotate with acid

syn-aryldiazotate substituents	$k_{-1}(s^{-1})$	pH	$k_A(s^{-1})$	pK_2
2-chloro-4-nitro	10	5.93	2.45	5.44
"	"	6.21	1.55	5.44
"	"	6.35	1.15	5.46
"	"	6.71	1.03	5.71
				Average = 5.51
2-nitro-4-chloro	16	6.16	4.61	5.73
"	"	6.35	2.60	5.63
"	"	6.70	1.82	5.81
"	"	7.16	0.59	5.93
				Average = 5.78

Values of K_1 were calculated form the above values of k_{-1} and k_1 from section 3.3.3 with equation (105) [120].

$$K_1 = k_1.K_w/k_{-1} \qquad (105)$$

This yielded values of 8.78 and 9.40 for the equilibrium between 2-chloro-4-nitro and 2-nitro-4-chlorobenzenediazohydroxide and their corresponding arenediazonium salts respectively. $(pK_1 + pK_2)/2$, also known as pH_m [128], is calculated to be as follows

(a) Equilibrium between 2-chloro-4-nitrobenzenediazonium cation and its aryldiazotate; $pH_m = 7.14$

(b) Equilibrium between 2-nitro-4-chlorobenzenediazonium cation and its aryldiazotate; $pH_m = 7.59$.

The known literature values of k_{-1} etc. refer to reactions performed at 20°C and at an ionic strength of 0.25 mol dm^{-3} and so our

measurements were carried out under the same conditions in order to determine the dependencies on the Hammett σ-constants of (i) log k_{-1}, (ii) pK_1, (iii) pK_2, (iv) pH_m and (v) the dependence of log k_{-1} on pH_m for the reasons explained later. The data used in these five correlations are compiled below.

Table 25

Compiled data for the equilibrium:

$$XArN_2^+ \underset{}{\overset{OH^-}{\rightleftharpoons}} XArN_2OH \overset{OH^-}{\rightleftharpoons} XArN_2O^- + H_2O$$

at 20°C, μ = 0.25 mol dm^{-3}

Substituent(s)	log k_{-1}	pK_2	pH_m	$\sigma^{97,144}$	pK_1
4-Cl	4.505	7.70	10.97[124]	0.23	14.24
3,4-Cl_2	3.477[130]	7.30[130]	9.83[124]	0.60	12.36
3-NO_2	2.728[130]	7.15[130]	9.10[124]	0.71	11.05
3,5-Cl_2	2.780[130]	7.05[130]	9.09[124]	0.74	11.13
3,5-Br_2	2.695[130]	7.00[130]	9.10[124]	0.74	11.2
3,4,5-Cl_3	2.484[130]	6.90[130]	8.75[124]	0.97	10.60
3-NO_2-4-Cl	2.29[130]	6.90[130]	8.58[124]	0.94	10.26
2,6-Cl_2-4-NO_2[120]	1.796	4.81	5.37	1.56	6.48
2,4-$(NO_2)_2$[119]	-	-	5.58	1.49	-
2-Cl-4-NO_2	1.00	5.51	7.14	1.17	8.78
2-NO_2-4-Cl	1.204	5.78	7.59	0.95	9.40

The values of the σ-constants of the 2-substituted groups utilised in Table 25 and Figs. 36-40 were those obtained from the reaction of arenediazonium cations with OH^- (section 3.3.3) because the effect of substituents on both reactions is expected to be similar. Sterba [130] noted that the σ-constants of the substituents in the 3,4,5-trichloro compound were somewhat less than additive

Figure 36 Hammett plot of log k_{-1} versus the σ-constants for the reaction of a series of syn-aryldiazohydroxides with acid

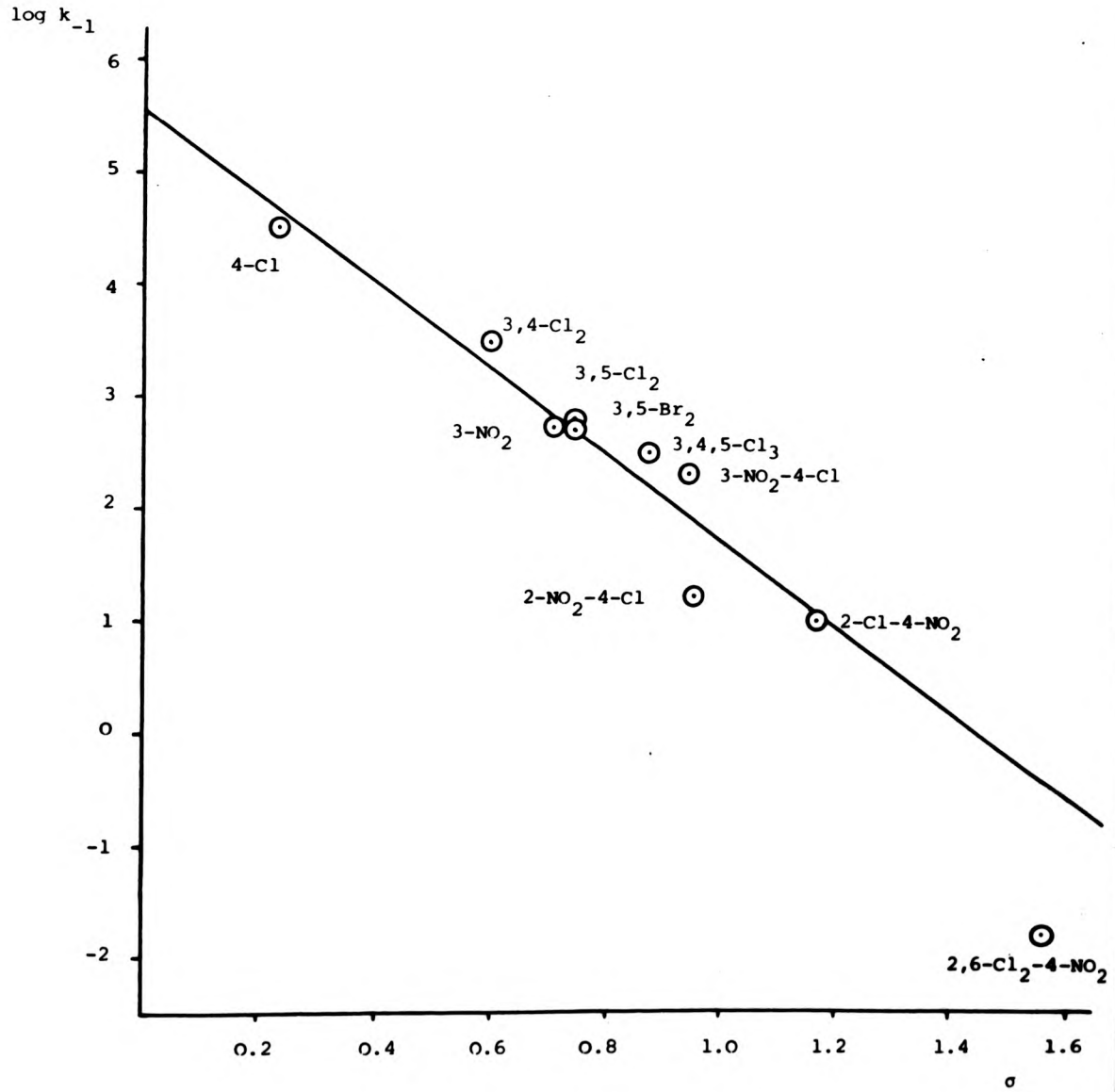
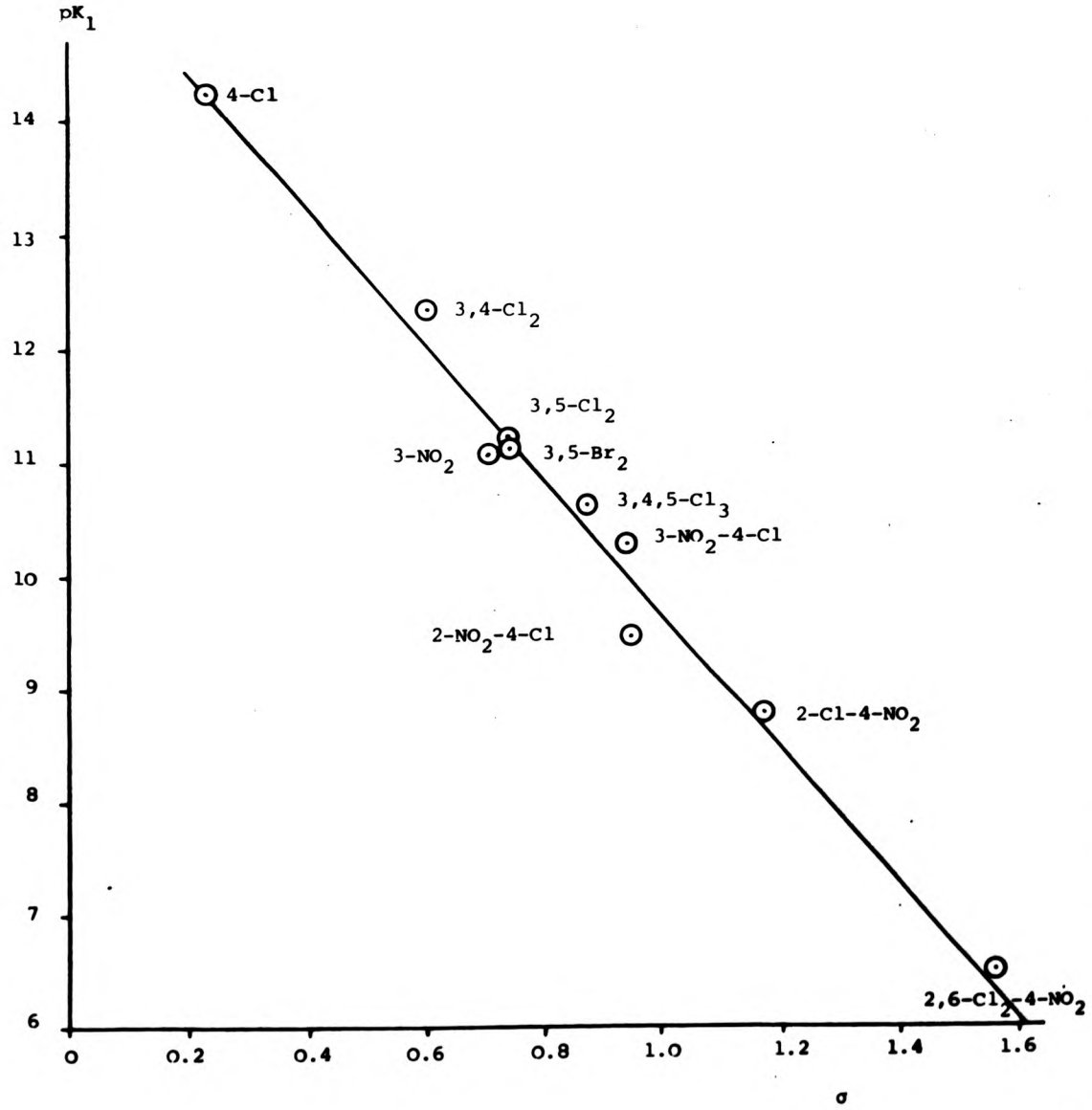


Figure 37 Plot of pK_1 against the σ-constants for the equilibrium between a series of syn-aryldiazohydroxides and the corresponding arenediazonium salts



and recommends the lower σ-value of 0.87 which gives better correlations between σ and log k_{-1}, pK_1, pK_2 and pH_m, and therefore it has been utilised in this work. (The data points from this compound correlate well in the remaining plot which does not involve σ-constants).

(i) The dependences of log k_{-1} on the Hammett σ-constants (Fig. 36) has a gradient ρ of -3.86 with a correlation coefficient of 0.956 when the data point corresponding to the 2,6-dichloro-4-nitro compound [120] (which has a substantially lower rate constant than expected) is omitted. Our value of ρ from the reactions of nine substituted compounds compares favourably with the value of -3.4 calculated by Sterba from six compounds [130]. The data points from the two 2-substituted compounds fit the plot well, indicating that the σ-constants used are appropriate and, because of the reasons discussed in section 3.3.3, do not affect the rate of reaction by interfering sterically with the departing OH^- group. In the one anomalous case, 2,6-dichloro-4-nitrobenzenediazotate, the combined effect of the two 2-chloro groups sterically hinders the reaction possibly by reducing solvation of the incipient cation.

(ii) The dependence of pK_1 on the Hammett σ-constant (Fig. 37) features the large ρ value of -5.86 and a very good correlation coefficient of 0.992 from nine data points. This correlation was obtained using values of K_1 calculated from both the literature [124,130] and from our values of k_1 and k_{-1} with equation (105). The large value of ρ indicates that the equilibrium constant of reaction (44) is stongly dependent on ring substituents and the figure of -5.86 is close to the difference between the ρ values from the dependences of log k_1 and log k_{-1} on the Hammett σ-constant,

Figure 38 Graph of pK_2 versus the Hammett σ-constants for the equilibrium between a series of syn-aryldiazohydroxides and their corresponding diazotates

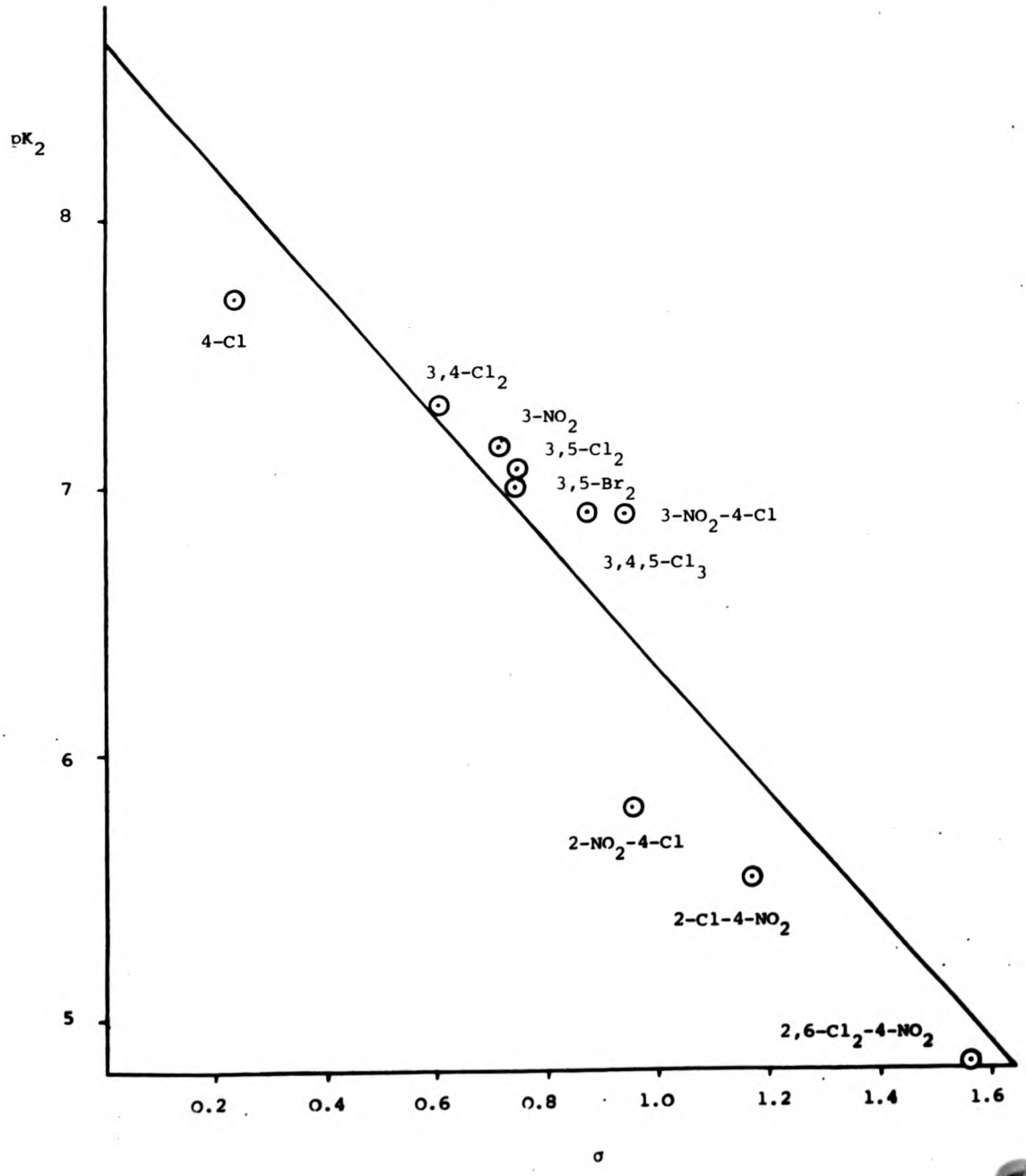


Figure 39

Dependence of the pH_m values of a series of arenediazonium cations on their σ-constants

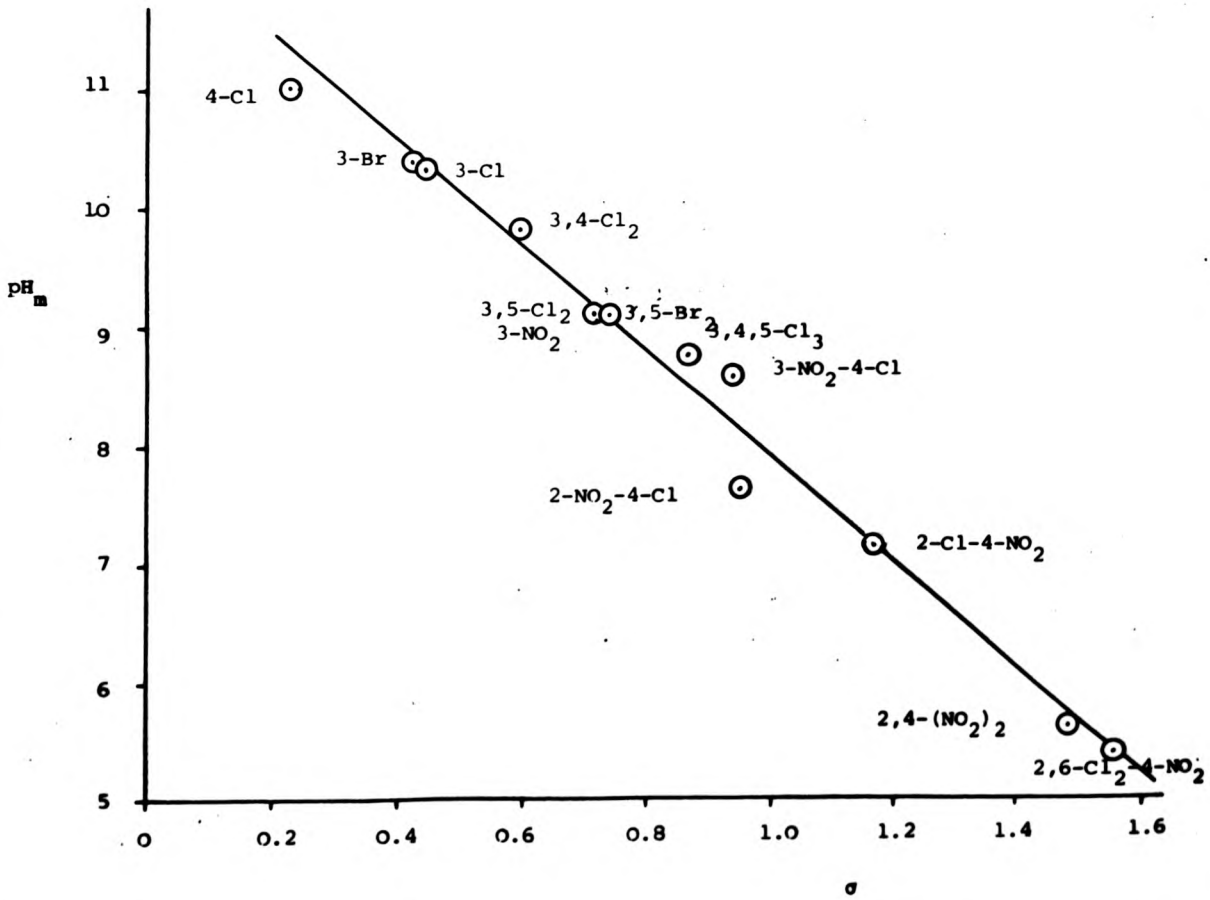
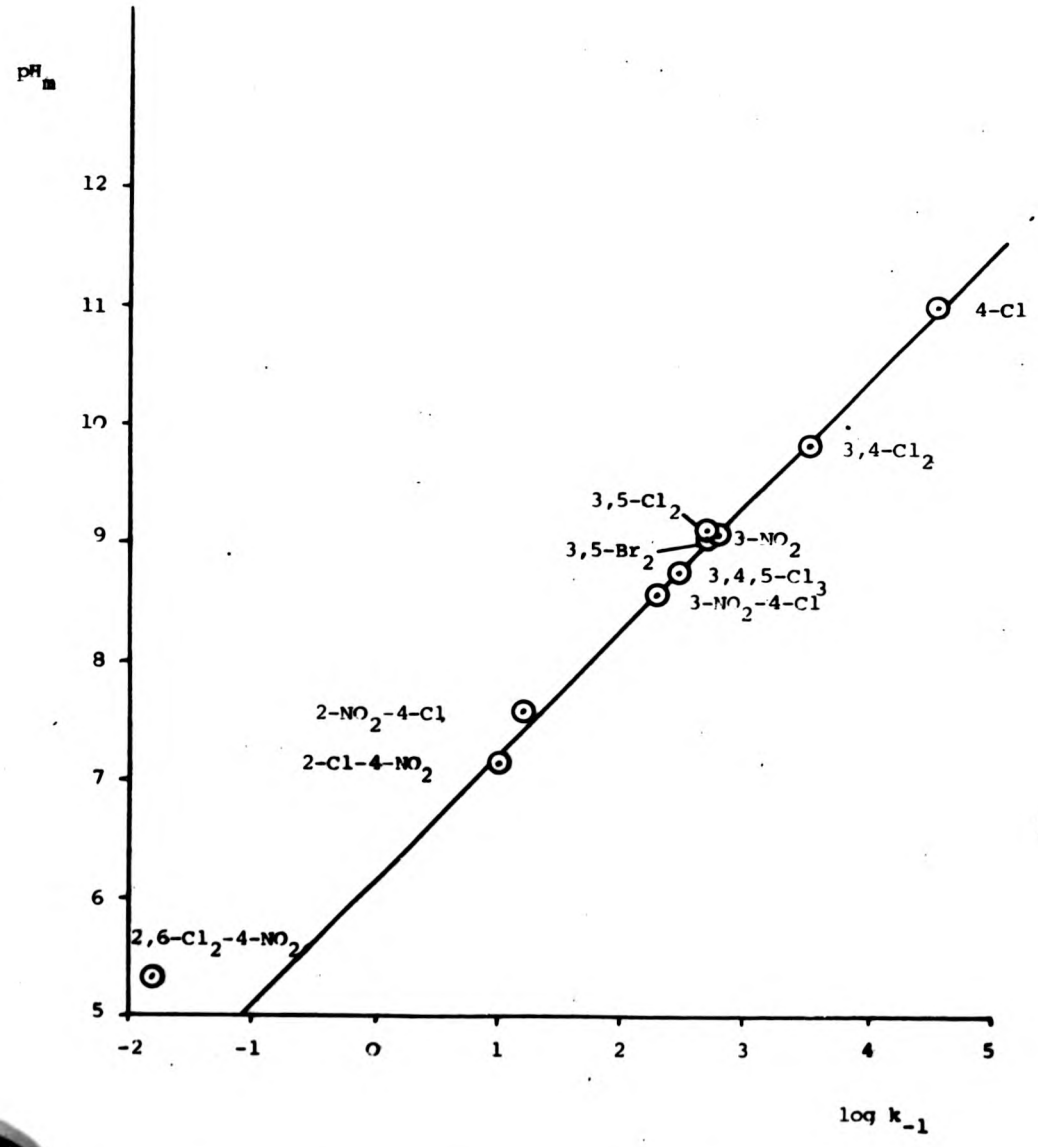


Figure 40 Graph of pH_m versus log k_{-1} obtained from the equilibrium between a series of arenediazonium cations and their corresponding syn-aryldiazotates



i.e. -3.86 - 2.26 = 6.12. It is interesting to note that whatever effects cause the anomalously low rate constants k_1 and k_{-1} for the forward and reverse of reaction (44) respectively of 2,6-dichloro-4-nitrobenzenediazonium ion, cancel each other and its data point in Fig. 37 fits the plot well.

(iii) The inclusion in Fig. 38 of our values of pK_2 and that from the equilibrium between 2,6-dichloro-4-nitrobenzenediazohydroxide and its aryldiazotate (45), together with the literature values, yields the reaction constant ρ of -2.42 (S.D. = 0.34) with a correlation coefficient of 0.925, which compares with a literature figure of ρ = -1.3. Both figures demonstrate that this equilibrium is less susceptible to ring-charge than (44) which is consistent with the generalisation [130] that large rate or equilibrium constants are less sensitive to substituent effects. (In this case, both k_2 and k_{-2} are larger than k_1 and k_{-1}).

(iv) The considerable effect of ring substituents on the equilibrium between arenediazonium cations and their corresponding aryldiazotates was demonstrated by the dependence of the pH_m values from twelve compounds on the Hammett σ-constants which affords a ρ value of -4.40 and a correlation coefficient of 0.988 (Fig. 39). This value is slightly larger than the figure of -3.33 quoted in the literature [130] which was calculated from only eight data points. Our reaction constant for pH_m compares quite well with that calculated from the relation:

$$pH_m = (pK_1 + pK_2)/2$$

thus the average of the two ρ values from the plots of pK_1 and pK_2 versus the σ-constants is (-5.86 - 2.42)/2 = -4.14 It was noted that the data point from the equilibrium of the 2,6-dichloro-4-nitro compound fitted satisfactorily with this plot, and its anomalous

behaviour is confined to the dependence of log k_{-1} on the σ-constants(Fig. 36). In order to ascertain whether this is due to the use of an incorrect σ-value, due either to steric effects or the failure of the additivity of the individual constants, the dependence of log k_{-1} on pH_m was plotted (Fig. 40).

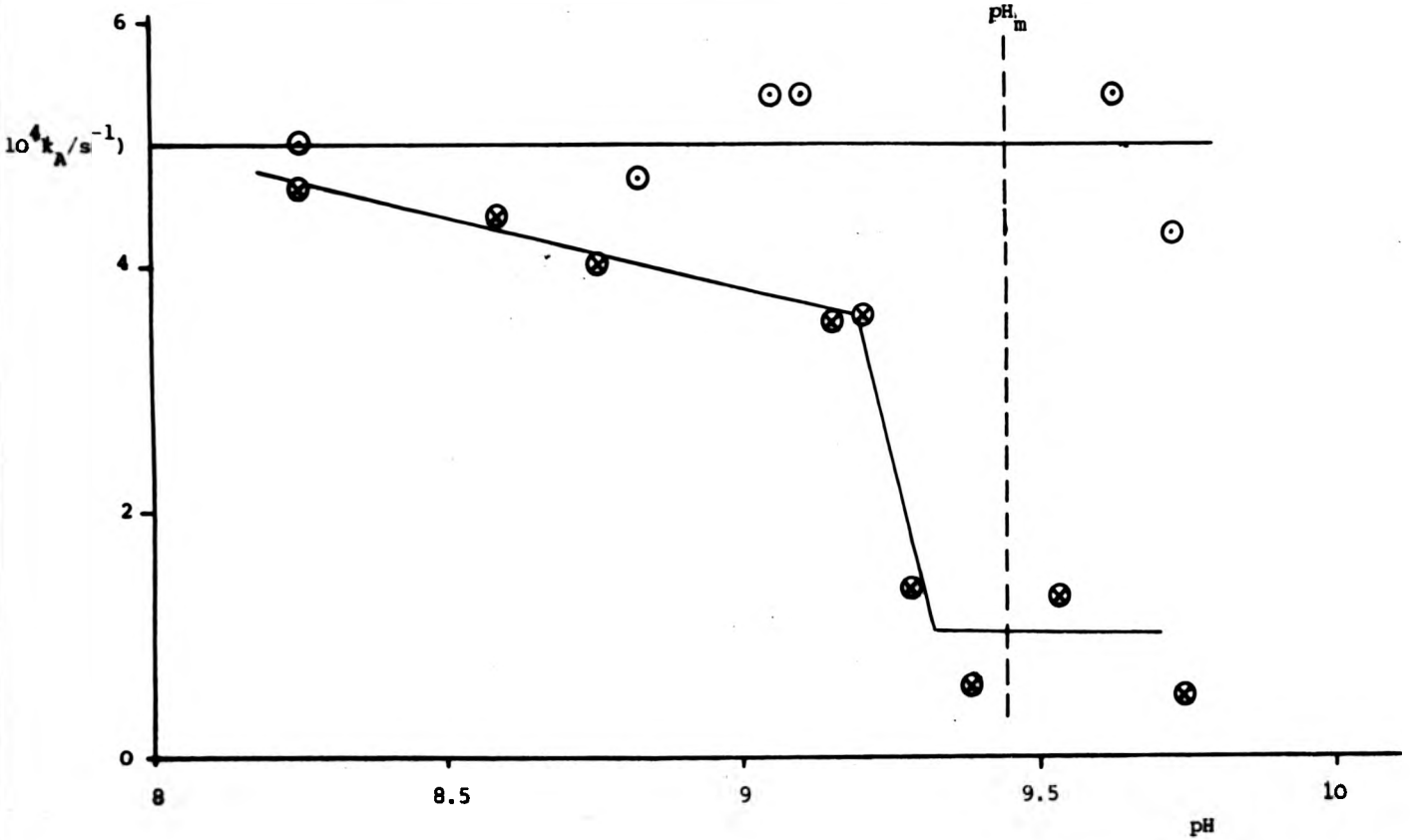
(v) The dependence of log k_{-1} and pH_m on the Hammett σ-constants have gradients of -3.86 and -4.40 respectively and so the gradient of 1.03 from the graph of log k_{-1} versus pH_m (Fig. 40) is similar to the predicted figure of 1.14 (-4.40/-3.86). Except for the data point from the 2,6-dichloro-4-nitro compound, an excellent correlation was obtained with a correlation coefficient of 0.988. The good fit to this plot by the value from the 3,4,5-trichloro compound demonstrates that the poor fit to the Hammett plots (Figs. 36-39) is due to the non-additivity of the σ-constants because, in Fig. 40, this effect is cancelled out. As a result of this, the most probable cause of any deviation from this plot is a steric effect. Poor fits to other linear free energy relationships by the data points from the reactions of 2,6-dichloro-4-nitro compounds are demonstrated later. A list of the ρ-values included in this section together with available literature values is given in Table 26.

Table 26

Compilation of our and the literature values of ρ

Hammett plot abscissa	ρ-values This work and literature values	Literature
log k_{-1}	-3.86	-3.4 [130]
pK_1	-5.86	-
pK_2	-2.42	-1.30 [130]
pH_m	-4.40	-3.39 [124]
		-3.15 [129]

Figure 41 pH- Dependence of the apparent rate constant of the reaction of anti-4-nitrobenzenediazotate with acid (⊗), and with acid (XXX) (⊙)



3.3.2 The reaction of anti-aryldiazotates with H^+

The reactions of anti-aryldiazotates in the pH region below the respective pH_m [121] values of their corresponding arenediazonium cations have been studied fairly extensively but, at higher pH, relatively little is known and so our investigations have concentrated in this region with anti-4-nitrobenzenediazotate as the example chosen because of (i) its ease of preparation (Section 2.1.7), (ii) the relatively convenient rates at which it reacts as opposed to the much more slowly reacting compounds having less strongly electron-withdrawing substituents and (iii) the 4-nitro compound has been investigated extensively in other pH regions by other workers [119,125,132].

The formation of the arenediazonium cation from anti-4-nitrobenzenediazotates in the pH range 8 - 10 was monitored spectroscopically by the appearance of an azo dye from the reaction of the product (4-nitrobenzenediazonium cation) with a suitable coupling compound (usually (XXX)). The apparent rate constants, k_A, were found to be independent of (i) the nature of the coupler, (ii) the coupler concentration and, in this pH range, (iii) the pH. This indicates that the rate-determining step of this reaction between pH 8.5 and 9.5 is the anti- to syn- isomerisation of the aryldiazotate and thus $k_A = k_{-3}$. The dependence of log k_A on pH is shown in Fig. 41.

To ensure that the coupler has no influence on the reaction, except to remove the arenediazonium cations, the reaction was repeated under similar conditions but in the absence of any coupler and the reaction was followed spectroscopically by the loss of anti-4-nitrobenzenediazotate. Below pH 9, rate constants were fractionally less than those obtained from the reactions in the presence of coupler, however, above pH 9 the values of k_A abruptly decrease with a rise in pH up to ca. pH = pH_m (9.44) at which the rate constants appear to

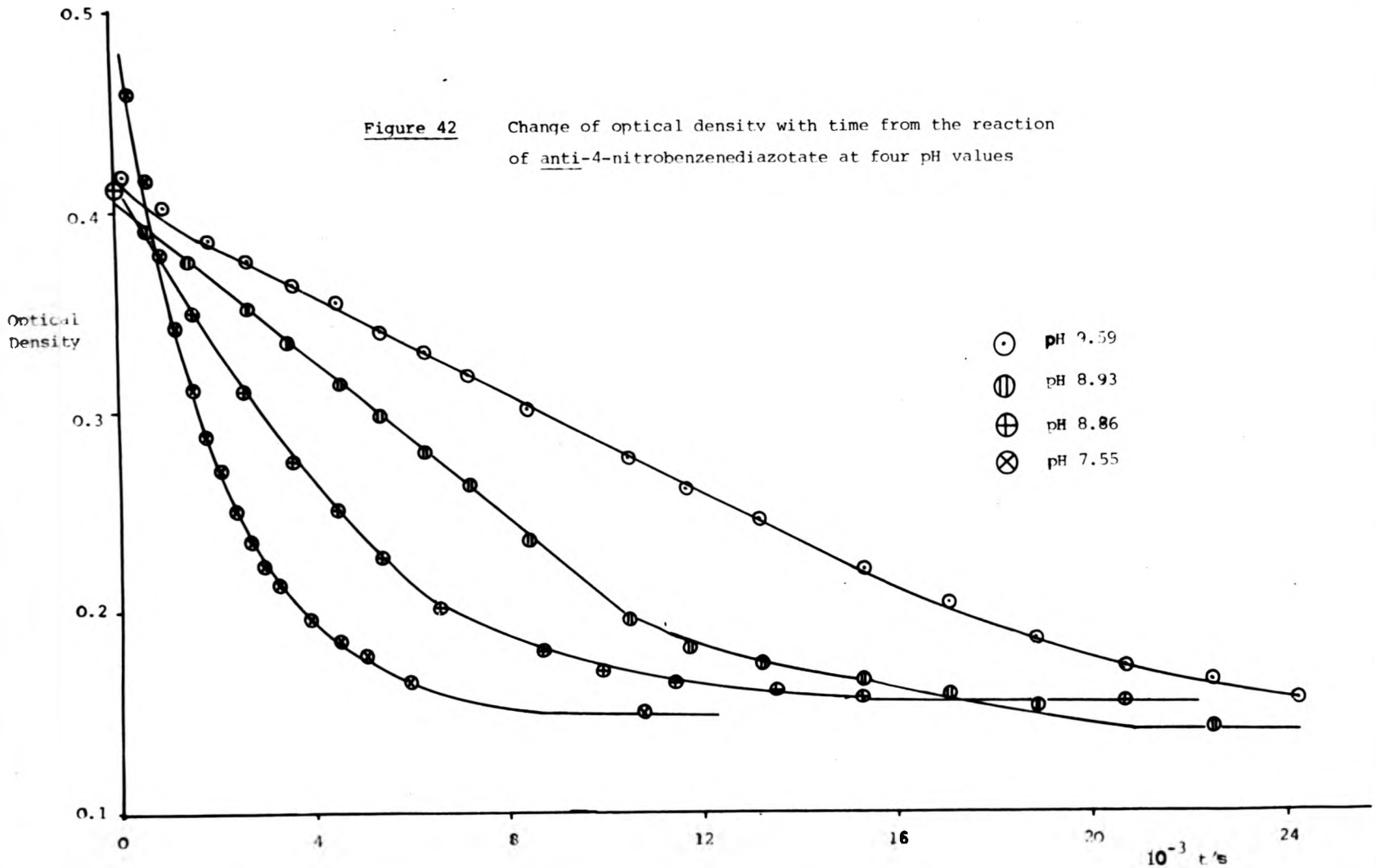


Figure 42 Change of optical density with time from the reaction of anti-4-nitrobenzenediazotate at four pH values

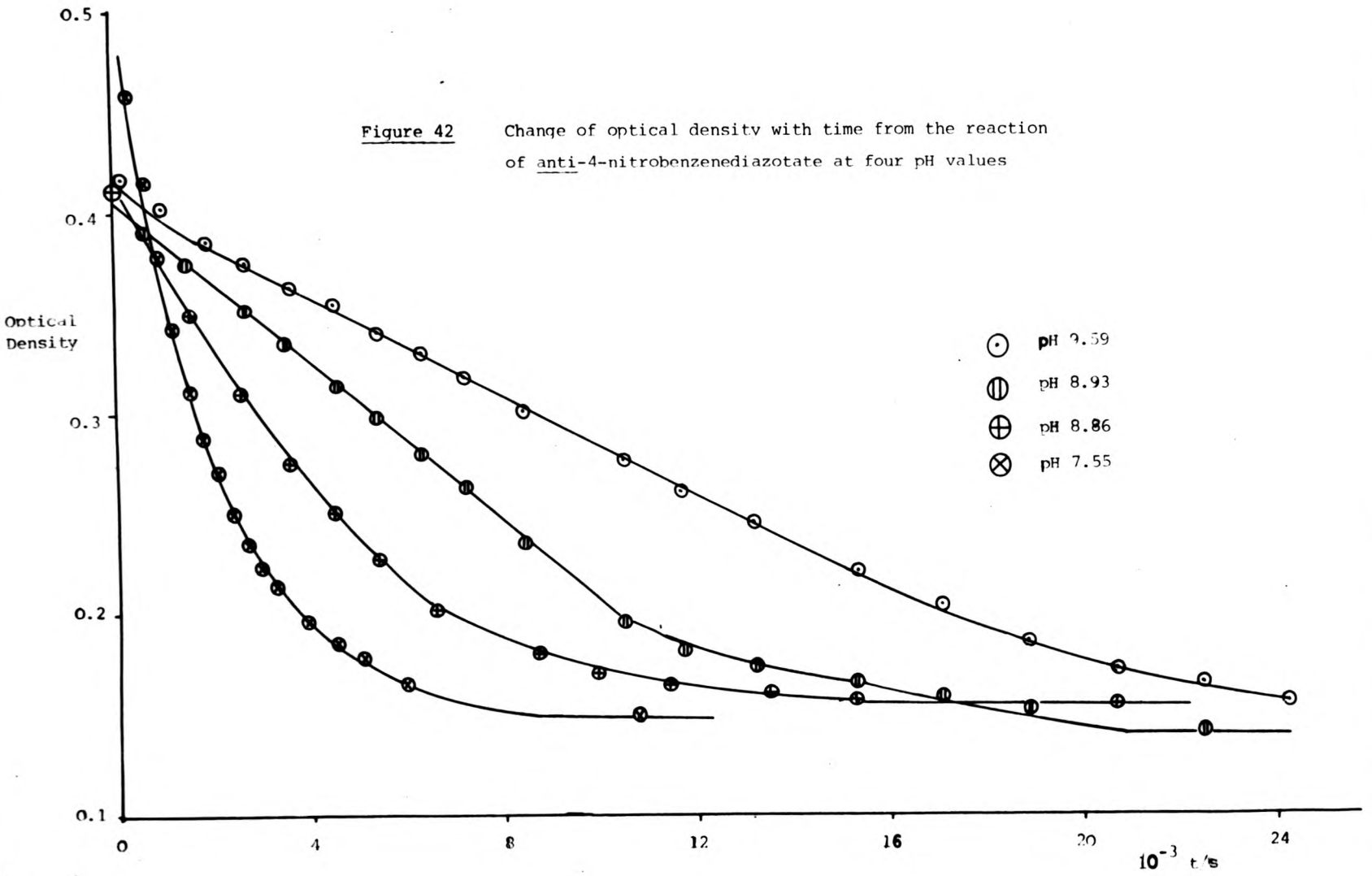


Figure 42 Change of optical density with time from the reaction of anti-4-nitrobenzenediazotate at four pH values

level off and become pH-independent. This data is included in Fig. 41.

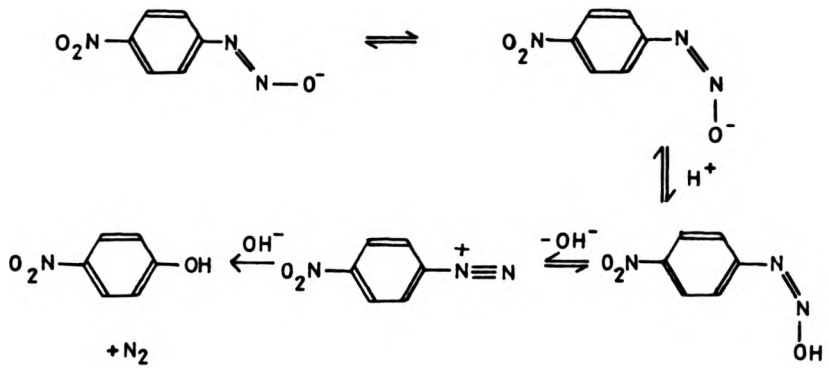
Inspection of a series of spectra taken during the reaction in the presence of coupler clearly reveals an isosbestic point which suggests that a simple 'A to B' type reaction occurs quantitatively. In the absence of coupler at pH > 9, this series of spectra do not yield a single isosbestic point, which indicates that the reaction is not of the simple, quantitative 'A to B' type and therefore may not be the same reaction as occurs in the presence of the coupling compound.

The optical density of a solution of the aryldiazotate was monitored at 305 nm and plotted against time at four pH values from pH 7.55 to pH 9.59 and a change from first- to zero-order reaction kinetics was found, see Fig. 42. This constitutes further evidence for a change in the reaction pathway.

The effect of various additives on this 'alternative pathway' were then investigated. Excess picric acid (a non-coupling phenol), pyridine (which increases the rate of certain coupling reactions by base catalysis) and 4-nitrophenol (the product from the thermal decomposition of 4-nitrobenzenediazonium cations) did not affect the rate of reaction whereas, removal of oxygen by flushing the solution with nitrogen increased the tendency to first-order kinetics at a higher pH than an aerated sample. Flushing with oxygen to increase its concentration gave zero-order kinetics at lower pH values than the N_2-flushed solution. This suggests that the 'alternative route' involves a species which is affected by the dissolved oxygen.

One problem we encountered in using the rapid scanning spectrometer was the photolysis of the arenediazonium cations and also the aryldiazotates in the intense xenon-arc lamp analysing beam. This did not occur with the conventional stopped-flow apparatus because much less intense, monochromated light passes through the solution.

The photolysis of anti-aryldiazotates have been investigated by Le Févre [128] but he was unable to identify the products although he observed that they were not phenolic and suggested that the photolysis may proceed via the syn-aryldiazotate. This indicates that the differences in rate constant and order of reaction brought about by the change in the reaction conditions may be due to a change from (105) to an alternative pathway involving the thermolysis of either the syn- or anti- aryldiazotate.



(105)

The occurrence of the two alternative pathways may be explained as follows:

the equilibrium between the syn- and anti-aryldiazotates is such that the concentration of the latter is much greater than the syn- form. The reaction in the presence of a coupling compound proceeds via the corresponding syn-aryldiazotate, the aryldiazohydroxide and the arenediazonium cation because as the last is rapidly removed by coupling, the isomerisation of the anti-compound becomes the rate-determining step, with a rate constant k_{-3}.

In the absence of any coupler, the small quantity of arenediazonium cation, which is in equilibrium with its precursor species, is removed

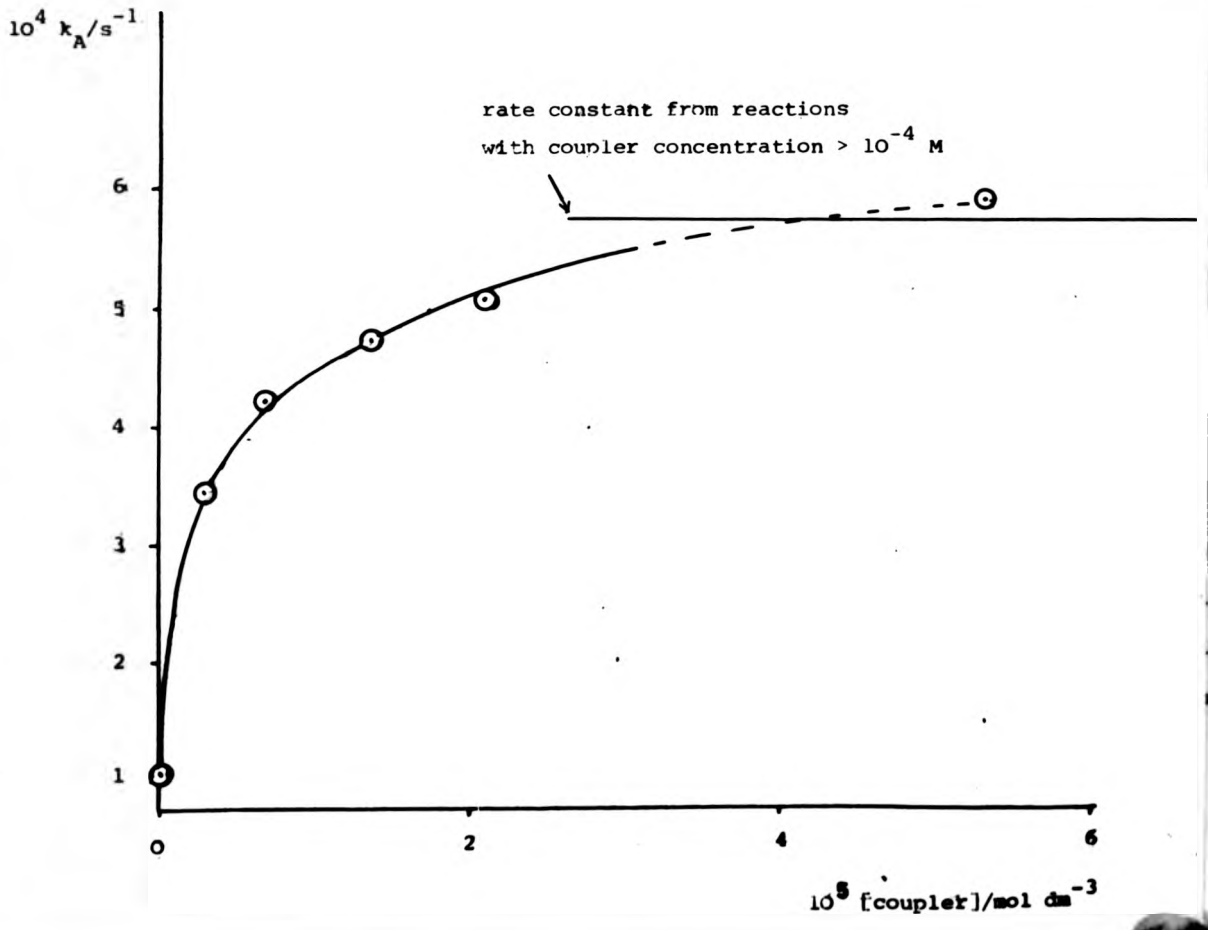
from the system only by its relatively slow thermal decomposition. At 50°C in dilute acid, the thermolysis rate constant is $8.6 \times 10^{-6} s^{-1}$ [35], although in an alkaline medium, the reaction is faster, very complicated and barely understood.

At pH < 9, the acid is sufficient to yield enough arenediazonium cation to ensure that (105) is the predominant pathway. At higher pH, the acidity is so low that insufficient 4-nitrobenzenediazonium cation is formed for this pathway to be significant and so the alternative slow thermal decomposition of either the anti- or syn-aryldiazotate becomes the principal reaction route.

Unfortunately, we were unable to identify the products from the thermal decomposition of anti-4-nitrobenzenediazotate at 60°C, although they are not phenolic. We have demonstrated that the presence of dissolved oxygen affects both the rate constant and the order of the reaction which indicates that a radical mechanism may be involved. No free radicals could be detected by e.s.r. from the thermolysis at room temperature but, from the photolysis at 195 K of its solution (ca. 0.001 M) in a glass consisting of aqueous LiCl (ca. 7 M) and NaOH (ca. 1 M) with a 200 W point source Xe/Hg bare arc light source for 110 minutes, a weak, but stable, e.s.r. singlet with a g factor of 2.001 and a line width ΔH_{ms} of 2.1 mT was recorded. The lack of fine structure was not unexpected as this is often absent in the e.s.r. spectra of semi-solids. The shape and linewidth suggest that the radical is unlikely to be either the nitrophenoxy (ΔH_{ms} = 0.7 mT) or nitrophenyl radicals. It is similar, however, to the singlet (ΔH_{ms} = 3 mT) obtained from the photolysis of benzenediazonium tetrafluoroborate at 77 K in methanol [14] but this species has also not been positively identified.

The reactions of anti-4-nitrobenzenediazotate in the pH range

Figure 43 Dependence of the apparent rate constant of the reaction of anti-4-nitrobenzenediazotate with acidic (XXX) on the coupler concentration



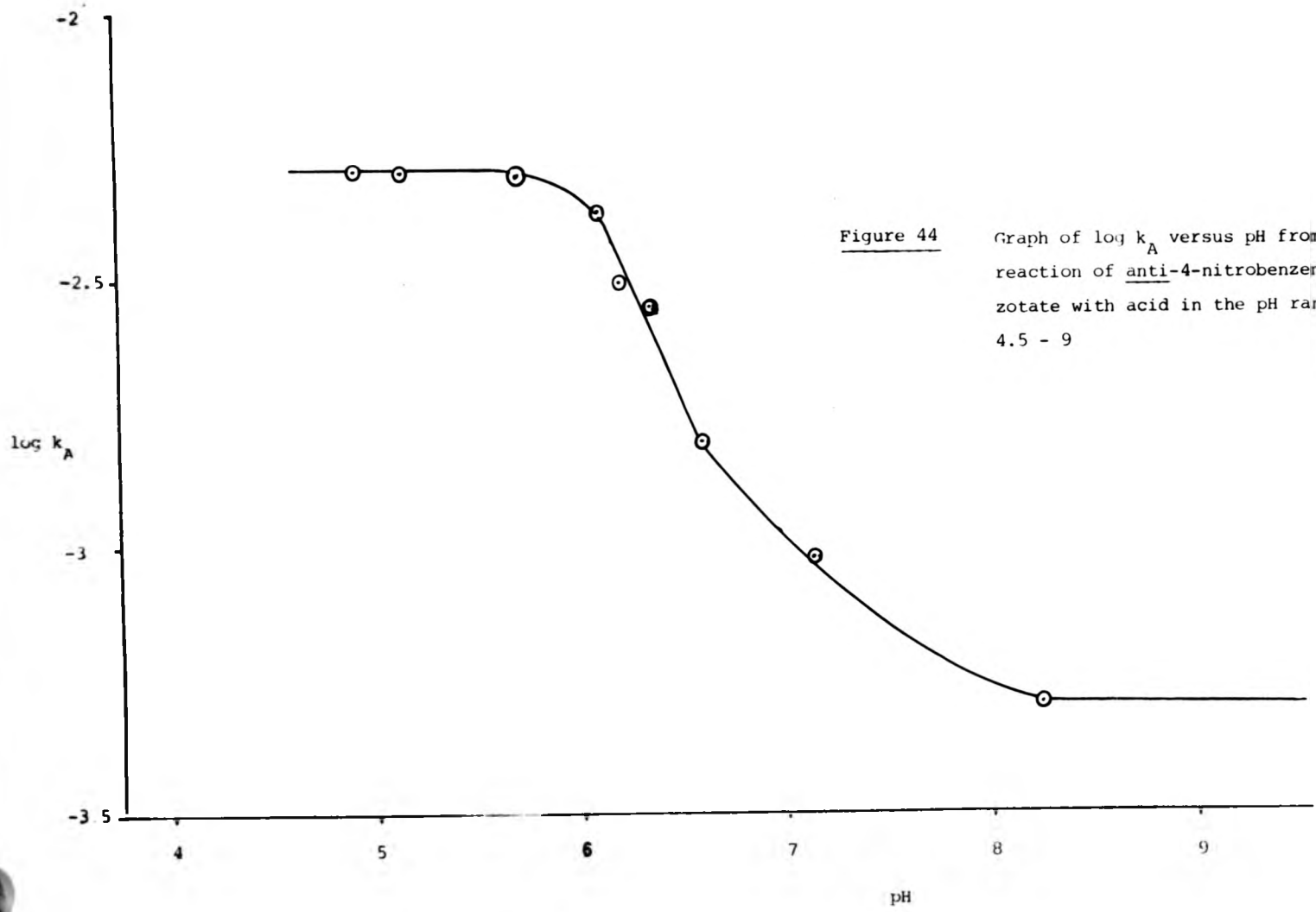


Figure 44 Graph of log k_A versus pH from the reaction of anti-4-nitrobenzenediazotate with acid in the pH range ca. 4.5 - 9

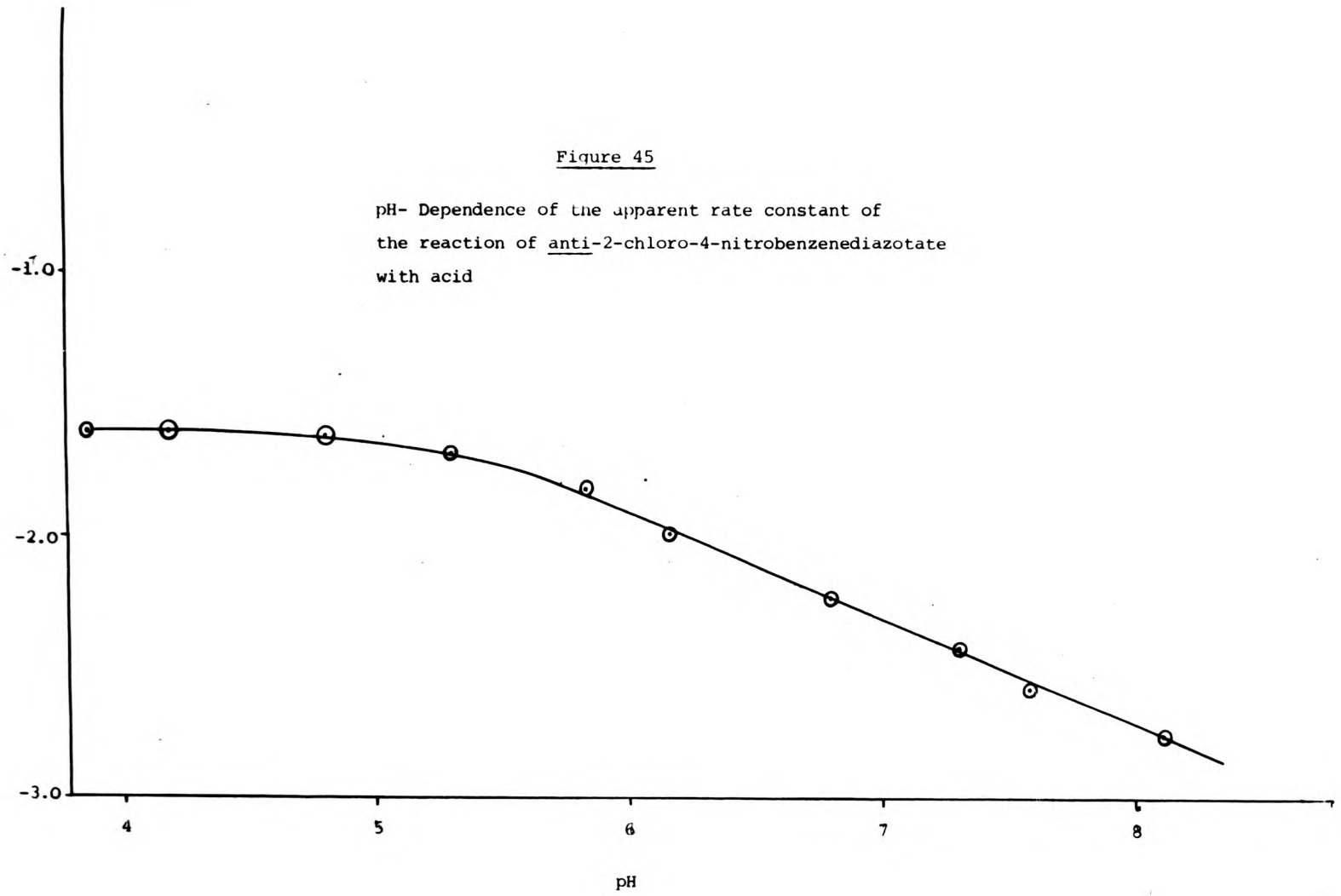
studied were performed with either an excess of, or in the absence of, coupling compound. The apparent rate constants of the reaction at pH 9.5 with intermediate concentrations of coupler were measured to obtain the dependence given in Fig. 43. This plot shows a rapid rise in rate constant with rise in coupler concentration up to approximatly equimolar concentrations of aryldiazotate and coupler (ca. 0.0005 M) above which the rate constant becomes independent of the coupler concentration.

The dependence of the apparent rate constant of the reaction of this compound with buffered coupler on a wider pH range was investigated and is depicted in Fig. 44. It is similar to the corresponding plot from the reaction of anti-2-nitro-4-chlorobenzenediazotate [127] except that, with the former, there is a wider plateau region between pH 8 - 10 where the rate determining step of the reaction is the anti- to syn-aryldiazotate isomerisation. The gradient in the region pH 6 - 7 is -0.90 which is somewhat less than the theoretical value of -1 (Section 1.4.2) and is possibly caused by the overlap between this region and the two plateaus above pH 8 and below pH 6. In this section of the plot, the rate-determining step is probably the formation of the anti-aryldiazohydroxide (48). The plateau below pH 6 is a result of a change of rate-determining step to the isomerisation of the anti- to the syn- aryldiazohydroxide (49) with a rate constant k_{-6} of $5.01 \times 10^{-3} s^{-1}$ at 295 K. (cf. The value measured by Lewis et al. of $4.8 \times 10^{-3} s^{-1}$ [123]).

The rate constant k_{-3} of the isomerisation of anti-4-nitro-benzenediazotate to its syn-isomer may be combined with the corresponding value of k_3 from section 3.3.4 to obtain a value of K_3.

Figure 45

pH- Dependence of the apparent rate constant of the reaction of anti-2-chloro-4-nitrobenzenediazotate with acid



$$k_3 = 7.9 \times 10^{-2} s^{-1}$$

$$k_{-3} = 5.03 \times 10^{-4} s^{-1}$$

$$K_3 = \frac{k_3}{k_{-3}} = \frac{[\underline{anti}\text{-form}]}{[\underline{syn}\text{-form}]} = 1.57 \times 10^2$$

This is somewhat less than the value of $K_3 = 600$, calculated indirectly by Littler [119].

Assuming that equilibrium (48) is rapid, equation (107) may be derived and from (107) [127] a value for K_5 of 6.75×10^{-7} mol dm^{-3} was calculated which is similar to the literature value of 7.2×10^{-7} mol dm^{-3} [125], all at 298 K.

$$k_A = k_{-6} [H^+]/(K_5 + [H^+]) \qquad (107)$$

The pH-dependence of the apparent rate constant of the corresponding reaction of 2-chloro-4-nitrobenzenediazotate with acid (Fig. 45) is markedly different to those obtained from the similar reactions of the 4-nitro- (Fig. 44) and 2-nitro-4-chloro- compounds (Fig. 4) [127]. Between pH 5.0 and 8.1, the gradient of this plot is -0.40 and below ca. pH 4.5 the rate constant becomes pH-independent. Comparison of these three graphs indicates that in this plateau reagion, the anti- to syn-aryldiazohydroxide isomerisation is the rate-determining step, i.e. $k_{-6} = 0.04\ s^{-1}$ which is of the same order as the same reaction of similar aryldiazotates, e.g. k_{-6} of the 2-nitro-4-chloro compound is $2.7 \times 10^{-2}\ s^{-1}$ [127]. A possible explanation for the slope of -0.40 is

that the two separate regions of the pH versus log k_A plot, corresponding to (a) the isomerisation of the anti-aryldiazotate to its syn-form and (b) the pH-dependent reaction of the anti-2-chloro-4-nitrobenzenediazotate with acid to the corresponding anti-aryldiazohydroxide as the rate-determining steps, merge into one straight line with a gradient intermediate between those expected from the two separate steps, i.e. 0 and -1 respectively.

Our rate constant (k_{-6} = 0.04 s^{-1}) of reaction (49) of the 2-chloro-4-nitro-compound lies reasonably close to the linear free energy relationship between the σ^--constants (2-substituent constants used were taken from Section 3.4.4) and the literature values of k_{-6};[127] however, our rate constant for the anti to syn isomerisation of 4-nitrobenzenediazohydroxide is substantially less than would have been predicted from this plot. One possible explanation for this anomaly is that, in this reaction, the 2-substituents exert substantial steric enhancement. Unfortunately, most other anti-aryldiazotates with 3- and 4- substituents react with acid by a different route; (reaction 55) and so k_{-6} cannot be measured. Rotation about the N-N bond in the N-nitrosamine tautomer is thought to be the mechanism of the isomerisation of aryldiazohydroxides [123] although it is unclear why 2-substituents sterically enhance this reaction.

3.3.3 The reaction of arenediazonium cations with OH^- ions to give syn-aryldiazotates

The equilibrium between a series of 3- and 4- substituted arenediazonium salts and their corresponding syn-aryldiazotates was first studied by Lewis et al [129] and more recently by other workers [124] as described in section 1.4.1. However, the correlation between rate constants and substituent constants do not include any information covering 2-substituted compounds. We have remeasured two values of k_1, the rate of the slower step of reaction (108):

$$ArN_2^+ + OH^- \underset{}{\overset{k_1 \text{ slow}}{\rightleftharpoons}} ArN_2OH \overset{k_2 \text{ fast, } OH^-}{\rightleftharpoons} \underset{\text{syn-aryldiazotate}}{ArN_2O^-} + H_2O \qquad (108)$$

and have also determined six new values of k_1, all at an ionic strength, μ, of 0.25 mol dm^{-3} and at 25°C. Ours and the literature values of k_1 are given in Table 27.

Table 27

Rate constants k_1 for the reaction of substituted arenediazonium salts with OH^- ions

Substituents	k_1 ($dm^3 mol^{-1} s^{-1}$) Our work	Literature values
4-nitro	3.7×10^5	2.0×10^5 (μ = 1M) [119] 5.4×10^5 (μ = 0.005M) [132]
2-nitro	3.37×10^5	
2-nitro-4-chloro	6.31×10^5	
2-chloro-4-nitro	1.67×10^6	
2,4-dinitro	8.64×10^6	7.5×10^6 [120]
4-diazonium	2.25×10^8	
2-chloro	5.04×10^5	
4-cyano	1.91×10^5	

The values of the second order rate constant k_1 given in Table 27 were calculated from the experimental pseudo-first order rate constant (k_A) with equation (76).

$$k_1 = \frac{k_A}{[OH^-]} \qquad (76)$$

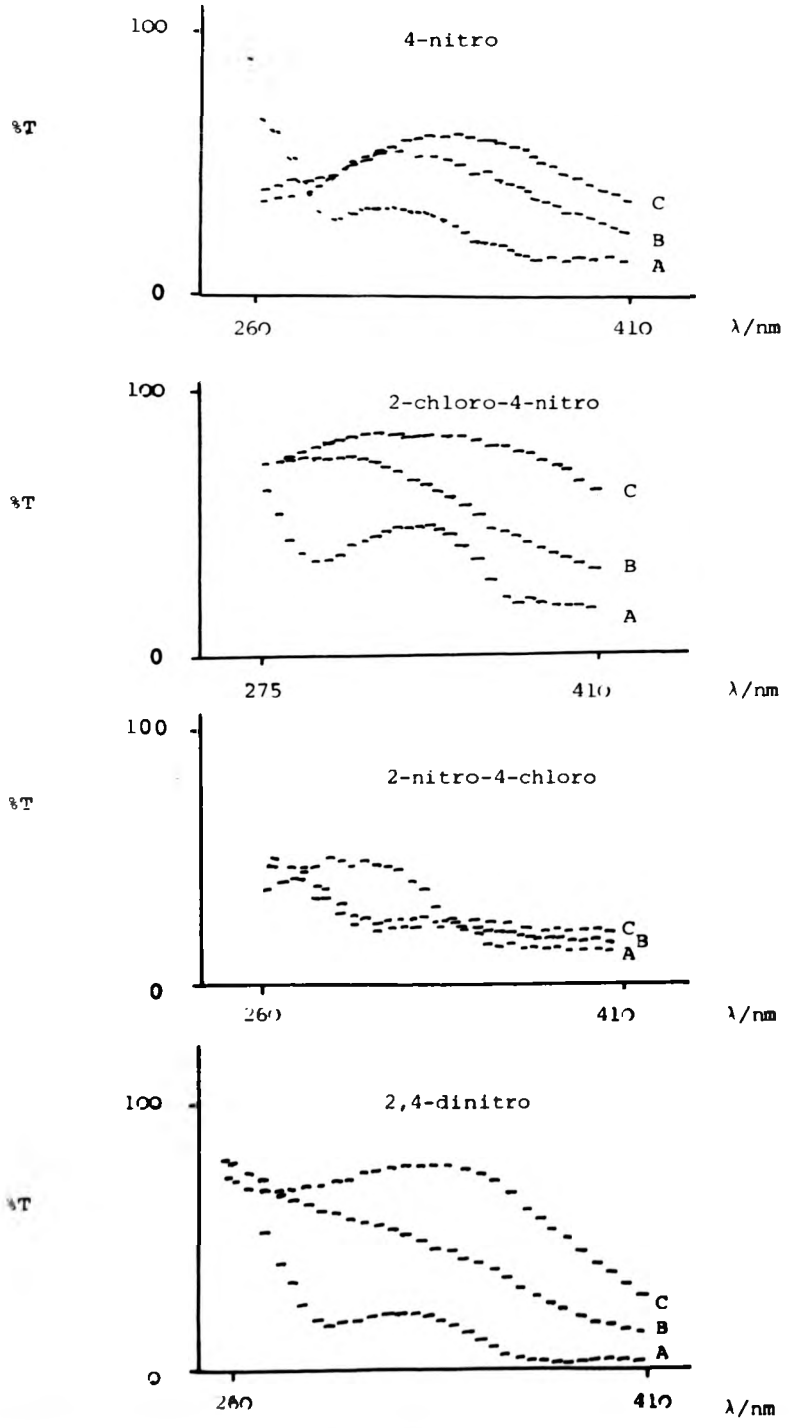
As described on p. 72, the hydrolysis of one nitro group of the 2,4-dinitrobenzenediazonium cation is compensated for by subtraction from k_A of the hydolysis rate constant, which is 0.79 s^{-1}, [120] before using equation (76). As expected from (76), log k_{obs} increases linearly with pH above pH_m, within experimental error. The values of k_A, k_1 and the gradients of the log k_A versus pH plots of four reactions of substituted arenediazonium salts with OH^- ion are given in Table 28.

Table 28

Data from the reactions of four substituted arenediazonium salts with OH^- ion above $pH = pH_m$

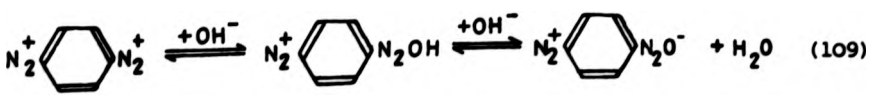
Substituents	pH	k_{obs} (s^{-1})	k_1 ($dm^3\ mol^{-1}\ s^{-1}$)	Gradient of log k_A/pH plot
4-nitro	9.36	8.8	3.84×10^5	1.06
	9.42	9.0	3.42×10^5	
	9.80	23.4	3.71×10^5	
	9.95	34.0	3.82×10^5	
2-nitro-4-chloro	9.14	8.50	6.16×10^5	0.905
	9.37	18.0	7.69×10^5	
	9.64	27.1	6.2×10^5	
	10.10	68.0	5.4×10^5	
2-chloro-4-nitro	8.50	5.3	1.7×10^6	1.102
	8.85	11.4	1.6×10^6	
	9.08	23.5	2.0×10^6	
2,4-dinitro	6.33	2.7×10^{-1}	9.4×10^6	0.740
	6.35	3.21×10^{-1}	1.1×10^7	
	6.72	4.5×10^{-1}	7.31×10^6	
	7.40	1.8	6.9×10^6	

Figure 46 U.v. spectra of (A) four arenediazonium cations and their corresponding (B) syn- and (C) anti-aryldiazotates. Ring substituents are given on each diagram.



Those syn-aryldiazotates with strongly electron-withdrawing substituents in the 2- and 4- positions rapidly isomerise to their corresponding anti-form and so cannot be isolated. As a result, their u.v. spectra have not been recorded previously. By the application of the rapid scanning spectrometer in conjunction with the stopped-flow apparatus, the spectra of four short-lived syn-aryldiazotates have been observed and are given in Fig. 46 with the corresponding spectra of their anti-forms and the arenediazonium cations.

Our experimental spectrum of syn-4-nitrobenzenediazotate is quite comparable with that calculated by Lewis et al [125]. This spectrum and also those of the 2-chloro-4-nitro and 2-nitro-4-chloro compounds may be observed at pH > 7.5 where $k_1 < k_3$, (k_3 is the rate constant of isomerisation of the syn- to anti-forms). However, the spectrum of syn-2,4-dinitrobenzenediazotate can be observed only at pH > ca. 9 because at pH < 9, $k_1 > k_3$ and only the spectral change corresponding to the change from the arenediazonium ion to the anti-aryldiazotate is observed with a rate constant of k_1. At high pH, the pH-dependent isomerisation rate constant k_3 is the same as at pH < 9, whereas k_1 increases ten-fold per unit rise in pH and at pH > ca. 9.5; $k_1 < k_3$ and so the spectral change due to the isomerisation of the syn-aryldiazotate to the anti-form is observed with a rate constant of k_3. The reaction of the arenediazonium salts with OH^- to give the syn-aryldiazotate in this pH region was too fast to be detected with the apparatus (i.e. $t_{\frac{1}{2}} \ll 5$ms). The spectrum of the syn-aryldiazotate of the 4-phenylene-bis-diazonium cation could not be observed because the reaction:



(109)

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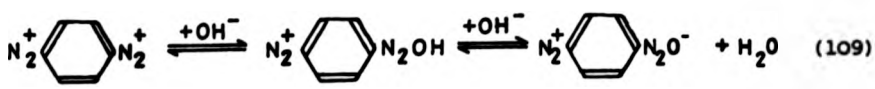

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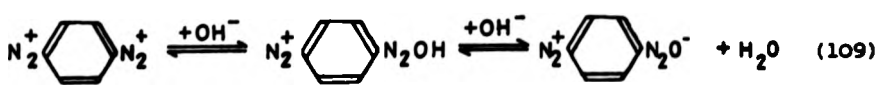
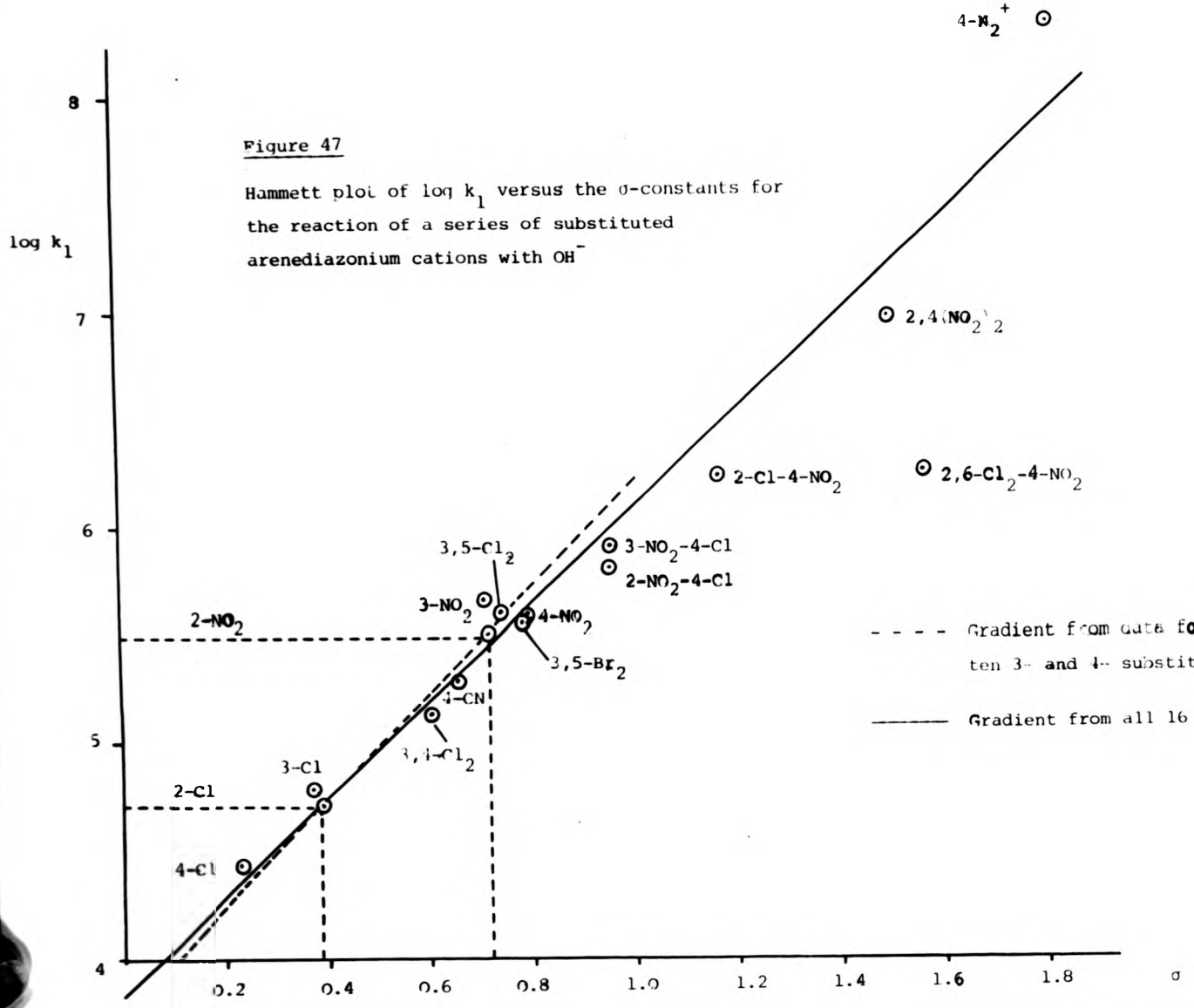


(109)

Figure 47

Hammett plot of log k_1 versus the σ-constants for the reaction of a series of substituted arenediazonium cations with OH^-



occurs only at pH < ca. 5 [113] (otherwise both diazonium groups are convertible into diazotate groups) and in this pH region $k_1 > k_3$ and therefore only the spectral change corresponding to the conversion of the arenediazonium salt to the anti-aryldiazotate may be followed with a rate constant k_3.

The spectra of the four syn-aryldiazotates (Fig. 46) are comparable with those recorded from the similar but more stable compounds without strongly electron-withdrawing substituents in the 2- and 4- positions [121]. In general, the spectra of the syn-forms have smaller ε_{max} and lower λ_{max} than their corresponding anti-isomers.

There are no standard Hammett σ-constants for 2-substituent groups because, unlike 3- and 4- substituents, they sterically influence the reaction site. In those cases where 2-substituent constants have been measured, there appears to be a different value, for a given substituent, for each of the reactions examined. In order to exploit the kinetic data obtained from 2-substituted compounds, the σ-constants for 2-Cl and 2-NO_2 were found by extrapolation of the Hammett dependence of log k_1 on the known σ-constants of the reactions of those ten compounds with no 2-substituents as in Fig. 47. This plot, which has a gradient of 2.48 and a correlation coefficient of 0.993, yielded the following σ-constants,

Substituents	σ-value
2-chloro	0.39
2-nitro	0.72

The value, σ = 0.72, of the 2-nitro substituent is comparable with that of 0.71 obtained from a coupling reaction by Sterba [120].

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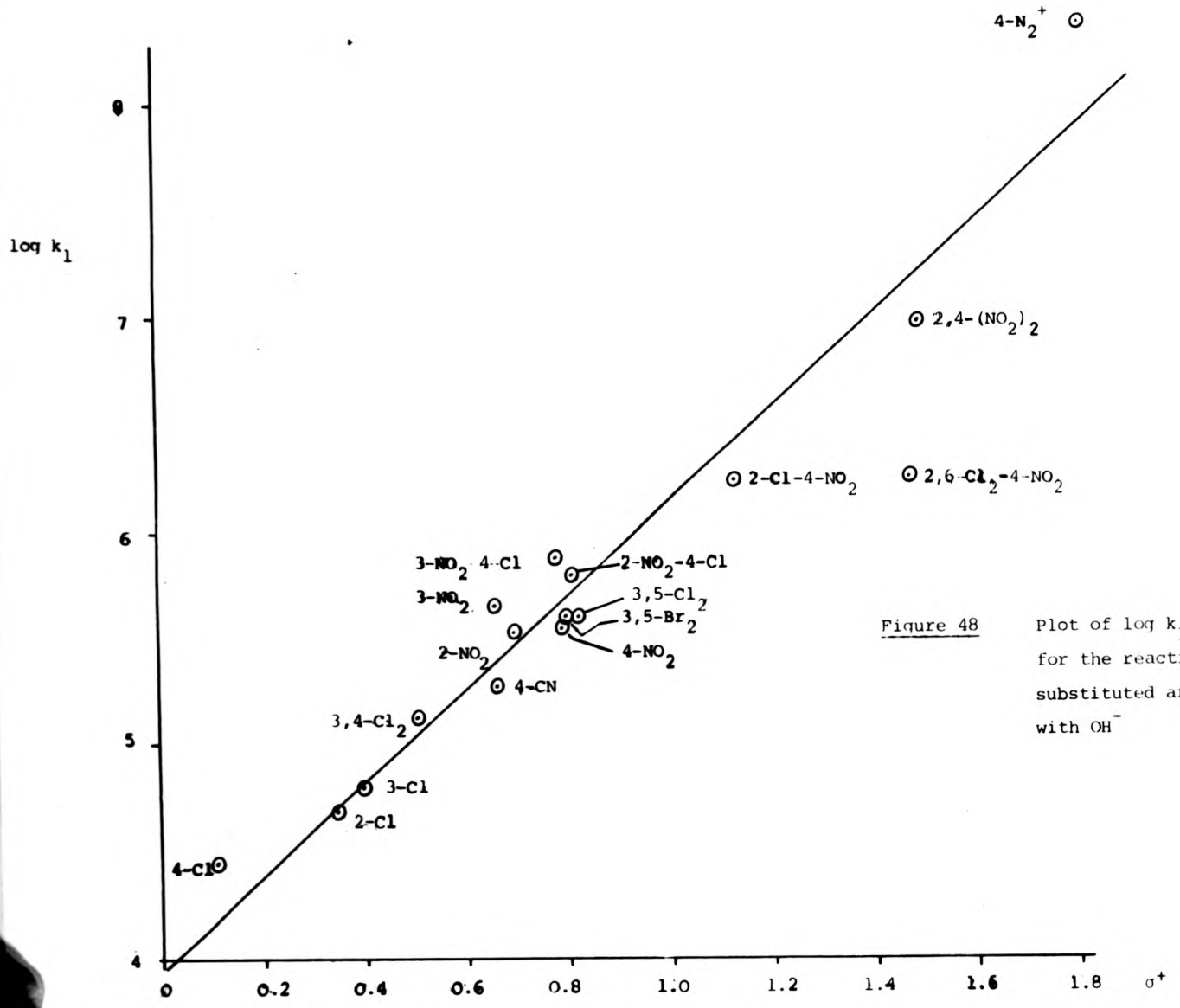


Figure 48 Plot of log k_1 against the σ^+-constants for the reaction of a series of substituted arenediazonium cations with OH^-

Our two values were used to calculate the σ-values of the six compounds with 2-substituents (assuming that the σ-constants are additive) in order to include these data in Fig. 47. The dependence of all sixteen values of log k_1 on the σ-values has a gradient ρ of 2.264 (S.D. = 0.115) and a correlation coefficient of 0.983.

Taft [133] obtained a better correlation between Sterba's rate constants (k_1) [124] of the reactions of arenediazonium cations with OH^- and σ_R^+ than with σ_R, both in dual parameter equations. To ascertain which series of substituents (σ or σ^+) give the better correlation with our rate constants, these were also plotted against the σ^+-substituent constants (Fig. 48). The σ^+ values for those arenediazonium salts with 2-substituents were found by the same method as described above for the analogous σ-constants. The values of σ^+ of the 2-Cl and 2-NO_2 groups were found to be 0.34 and 0.70 respectively. No improvement in the correlation was achieved by incorporating σ^+-constants, the gradient of the dependence of the sixteen values of log k_1 on σ^+ being 2.183 (S.D. = 0.125) with a slightly smaller correlation coefficient, of 0.978, than the corresponding value from the dependence on the σ-constants. The failure of the σ^+ constants to improve the correlation indicates that there is very little electron transfer to the diazonium group from the substituent group, which is not unexpected since all the substituents on the arenediazonium cations studied here were of the electron-withdrawing type. An improved correlation may have resulted if the reaction of base with arenediazonium ions having electron-donating substituents were included.

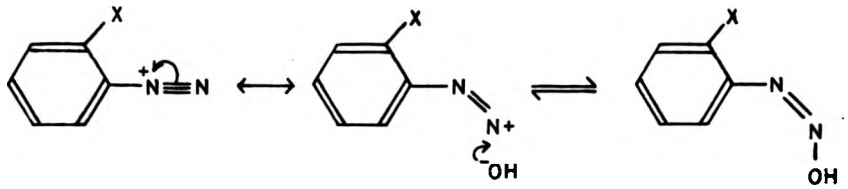
The positive ρ value indicates that there is an increase in

electron-charge density on the atom adjacent to the benzene ring during the reaction, i.e. the positive charge of the diazonium group becomes neutral in the diazotate. The size of ρ (2.264) is similar to the literature value of 2.06 [129] and suggests that substituents do not have large electronic or steric effects on the reaction centre although, the exceptionally low value of k_1 for the reaction of 2,6-dichloro-4-nitrobenzenediazonium cations with base is probably due to a steric effect.

A substituent constant comprises three effects, (i) the inductive effect, (ii) the mesomeric donation or withdrawal of electrons and (iii) the steric effect. Substituent groups at the 3- and 4- ring positions exert negligible steric effects on the reaction, while groups in the 2-position often have large steric effects although these differ from reaction to reaction and therefore there are no standard 'ortho-substituent constants, [133]; consequently we have measured them both for this particular reaction and also for the isomerisation reaction in section 3.3.4. Substituent constants of the 2-Cl and 2-NO_2 groups from 0.2 to 2 and from 0.3 to 5 respectively have been measured (see Table 6 p 46) but presumably, the σ-values of 2-substituents in reactions where they have small steric effects will be similar to those for the equivalent 4-substituent group, (e.g. 0.23 and 0.78 are the Hammett σ-constants of the 4-Cl and 4-NO_2 groups respectively).

Our values for the 2-Cl and 2-NO_2 groups in this reaction are fairly similar to these values and also to Taft's aliphatic σ-constants, which make no steric contribution to the overall σ-values [146] (see Table 6), indicating that the 2-substituents in this particular reaction have only small steric effects. If the OH^- ion approaches the diazonium group at the opposite side to the

2-substituent as in (110), then no steric effect would be expected.



(110)

If, however, the arenediazonium cation is substituted in both the 2- and 6- positions, as in 2,6-dichloro-4-nitrobenzenediazonium ion, then, due to the proximity of one of the substituents adjacent to the diazonium group, the approach of the OH^- ion could be hindered sterically, resulting in a lower value of k_1 than expected from the linear free energy relationship (Fig. 47) and this is found to be the case. Although the OH^- ion is relatively small, it is thought to approach the diazonium group as a much bulkier solvated species which desolvates before the formation of the aryldiazohydroxide [124].

3.3.4 The effect of ring-substituents on the isomerisation rate constants of syn-aryldiazotates to their anti-form

The rate constants of the isomerisation of substituted syn-aryldiazotates to their anti-forms were measured and in most cases found to be close to the literature values, where these are available. The relatively small discrepancies may be due to the variety of ionic strengths and temperatures utilised by other workers [132, 129]. All of our results and the majority of literature values of the rate constants given in Table 29 were obtained from measurements taken at an ionic strength (μ) of 0.25 mol dm^{-3} and at 25°C.

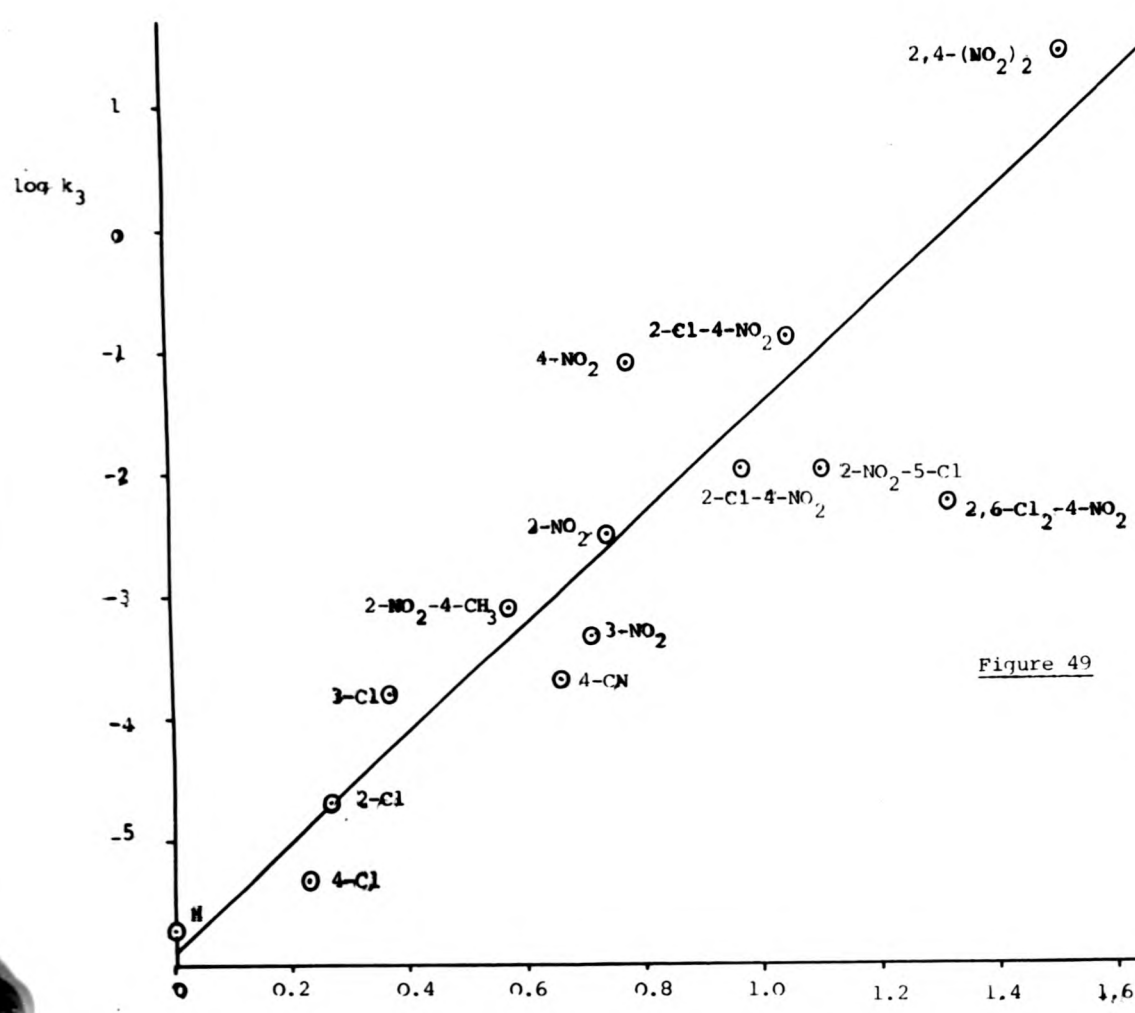


Figure 49 Graph of log k_3 versus the Hammett σ-constants from the isomerisation reaction of a series of syn-aryldiazotates to their corresponding anti-forms

Table 29

Rate constants k_3 of the isomerisation of syn-aryldiazotates to their corresponding anti-forms

Substituents	Rate constants k_3 (s^{-1}) (this work)	Literature values of k_3 (s^{-1})
4-Cl		5.0×10^{-6} [129]
4-CN	1.98×10^{-4}	
2-Cl	6.0×10^{-5}	
3-NO_2	4.53×10^{-4}	
3-Cl	1.57×10^{-4}	
2-NO_2	3.3×10^{-3}	1.5×10^{-3} [127]
4-NO_2	7.9×10^{-2}	6.2×10^{-2} (μ = 0.005 mol dm^{-3}) [132]
H		2.0×10^{-6} [129]
2,4-$(NO_2)_2$	24.0	20.9 [127]
2-Cl-4-NO_2	0.13	0.032
4-Cl-2-NO_2	1.0×10^{-2}	4.3×10^{-3}
2,6-Cl_2-4-NO_2		5.5×10^{-3}
2-NO_2-4-CH_3		7.8×10^{-4}
2-NO_2-5-Cl		1.0×10^{-2}

As in the previous section, the 'ortho-substituent constants [133] were obtained from the dependence of log k_3 from the reactions of 3- and 4- substituted aryldiazotates on the Hammett σ-constants [97] and found to be

$$\sigma \text{ (2-chloro)} = 0.27$$

$$\sigma \text{ (2-nitro)} = 0.74$$

The plot of log k_3 against σ (Fig. 49) for the 3- and 4- substituted

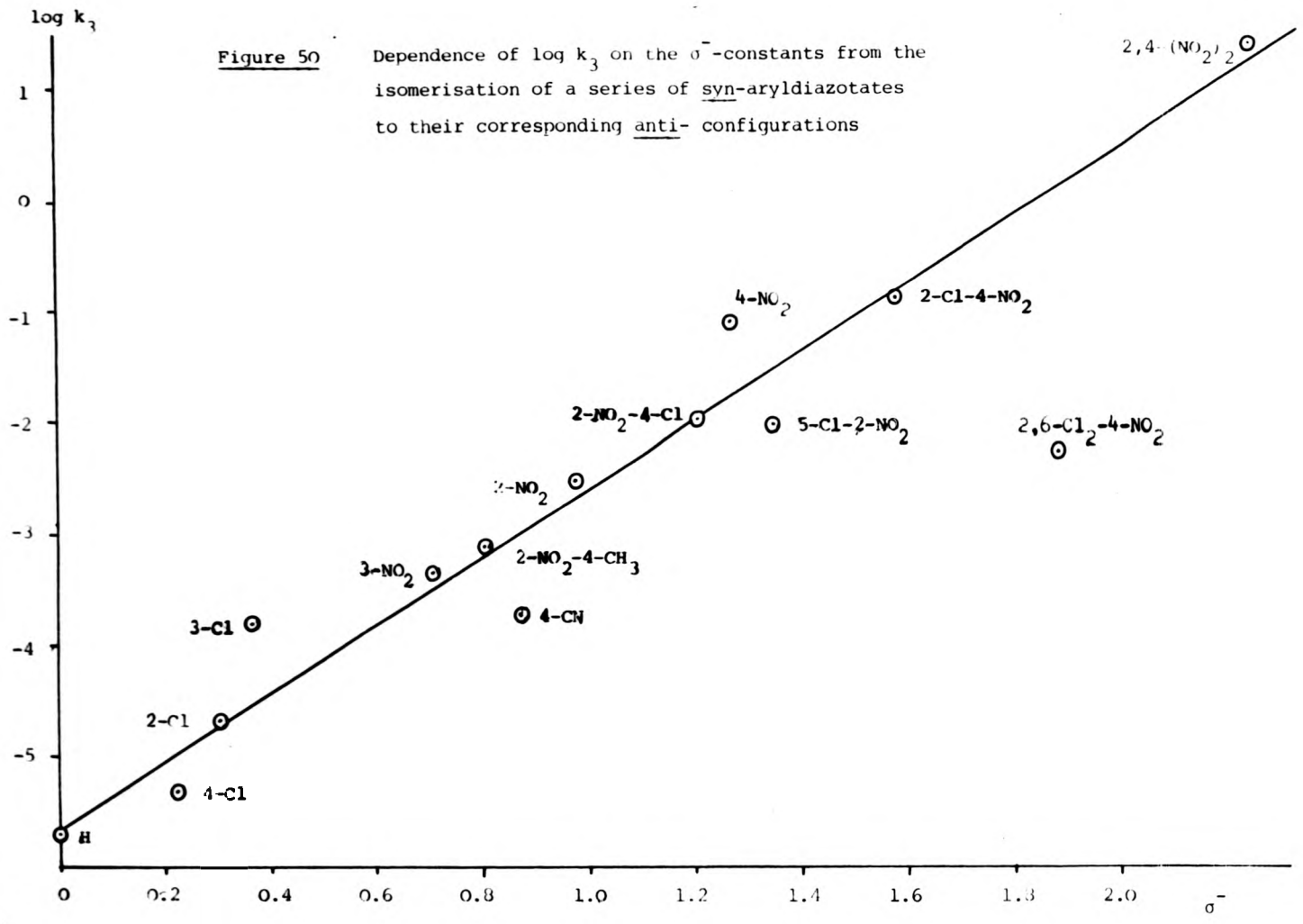


Figure 50 Dependence of log k_3 on the σ^--constants from the isomerisation of a series of syn-aryldiazotates to their corresponding anti- configurations

aryldiazotates has a gradient of 4.65 and a correlation coefficient of 0.878. A slightly better correlation was found when the data was plotted against σ^--constants with a gradient of 3.36 and a correlation coefficient of 0.934 (Fig. 50). The two σ^--substituent constants of the 2-chloro and 2-nitro groups were determined as:

$$\sigma^-(\text{2-chloro}) = 0.31$$

$$\sigma^-(\text{2-nitro}) = 0.98$$

These two σ and σ^- substituent constants were used to calculate the corresponding values of the other 2-substituted compounds in order to incorporate their values of log k_3 in Figs. 49 and 50. (As usual, the substituent effects were assumed to be additive). Good linear correlations were obtained and we noted that our values of k_3 from the isomerisation of the 2-chloro-4-nitro and 2-nitro-4-chloro-benzenediazotates correlate better with the rest of the data in Figs. 49 and 50 than the quoted literature values,[127] however the corresponding data point from the 2,6-dichloro-4-nitro compound lies well away from the linear free energy relationship with a lower value of k_3 than would have been predicted.

The dependence of log k_3 on σ has a gradient (ρ) of 4.458 (S.D. = 0.460) with a correlation coefficient of 0.946 from thirteen data points. A much improved correlation is found from the dependence of these values on the σ^--constants with a gradient (ρ) of 3.072 (S.D. = 0.195) and a correlation coefficient of 0.979. The correlation coefficient from all the data in Table 29, including those from the 2-substituted compounds, were in both cases better than the respective values calculated with only the six 3- and 4-substituted compounds.

The substantially better correlation with the σ^- substituent constants (than with the Hammett σ-values) indicates that there is

aryldiazotates has a gradient of 4.65 and a correlation coefficient of 0.878. A slightly better correlation was found when the data was plotted against σ^--constants with a gradient of 3.36 and a correlation coefficient of 0.934 (Fig. 50). The two σ^--substituent constants of the 2-chloro and 2-nitro groups were determined as:

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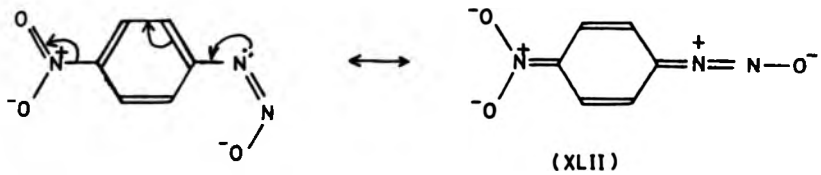
The substantially better correlation with the σ^- substituent constants (than with the Hammett σ-values) indicates that there is

some electron transfer to electron-withdrawing substituents (such as 4-nitro) from the diazotate group, i.e.

(111)

or:

(XLI)



(112)

(XLII)

(XLII) has been suggested as the most likely reaction intermediate (or transition state) in the isomerisation of aryldiazotates having strongly electron-withdrawing substituents although those without such groups isomerise via the species (XLI) [119]. Littler has suggested (from less data) that the Hammett σ-constant (rather than the σ^--constants) yield the better correlation [119] but, Sterba [127] has successfully used the σ^--constants with the Yukawa-Tsuno equation [150] to obtain a ρ value of 2.1, which is rather less than our figure of 3.072 calculated from many more data. The magnitude of ρ reflects the extent of the formation of (XLI) or (XLII), i.e. the greater the electron-withdrawing power of the substituent, the larger is the tendency towards structures of the type (XLII) which results in an increased isomerisation rate constant. This figure (3.072) is larger than the reaction constant of the reaction of hydroxyl ions with substituted arenediazonium salts (ρ = 2.264) and the isomerisation of aryldiazohydroxides (ρ = 1.1) [127] which is consistent with an increased charge sensitivity

of the slowest reaction. A positive ρ value usually indicates an increase in the electron density of the atom (of the reacting group) adjacent to the benzene ring but in (XLI), this atom, denoted N(1), remains neutral during the isomerisation. In (XLII), N(1) becomes initially positively charged and then, after 'overturning of the positively charged nitrogen', [127] the electron charge density on N(1) increases and it returns to neutrality.

As shown in the last section, the σ-constants for the 2-chloro and 2-nitro groups are rather similar to the Hammett σ-values of the 4-chloro and 4-nitro groups of 0.23 and 0.78 respectively. Again, our σ^- value for the 2-NO_2 group compares quite well with that of the 4-NO_2 substituent of 1.27. This suggests that neither of the 2-substituents has a large steric effect on the reaction site (the diazotate group). If the reaction were to proceed via (XLII) then a substituent in the 2-position will be sufficiently distant from the diazotate group so as not to interfere sterically with its formation or isomerisation and thus the values of the 2-substituent constants will be similar to the corresponding constants of 4-substituents.

The unexpectedly low rate constant k_3 of the reaction of <u>syn</u>-2,6-dichloro-4-nitrobenzenediazotate to its <u>anti</u>- configuration suggests that the second 2-substituted chloro-group sterically hinders the isomerisation reaction which is feasible <u>only</u> if (XLI) is the reaction intermediate in which one of the 2-chloro groups will be sufficiently close to the diazotate group to interfere sterically with it.

4. Conclusions and suggestions for further work

4.1 Conclusions

This work has been divided into three sections the results from which are as follows:

(i) The structure of disodium *syn*-benzenediazotate-4-sulphonate was determined by X-ray crystallography. The diazotate group was shown to have a *cis*oid configuration and the plane of this group subtends an angle of 69.1° with that of the benzene ring.

(ii) The rate constants of coupling reactions are known to be affected by a number of factors including the pH, ionic strength, temperature and nature of the two reactants. We have further elucidated the mechanism of this reaction by the observation of the effects of alteration of one variable at a time. The pH-dependence of the rate constant of the reaction of 4-chlorobenzenediazonium cation with sodium 2,3-dihydroxynaphthalene-6-sulphonate (XXX) may be divided up into four regions. Below *ca.* pH 8, the rate constant increases ten-fold per unit rise in pH due to the ionisation of the unreactive coupler to the reactive singly-ionised form. At *ca.* pH 8.5, there is a small plateau caused by the almost complete ionisation of the coupler and above this region the rate constant increases again due to ionisation of the second hydroxyl group. Above pH 10 the plot levels off and the apparent rate constant drops at even higher pH, probably because of the formation of the non-coupling 4-chlorobenzenediazotate from the arenediazonium salt. This reaction is further complicated in the presence of a borax buffer by an equilibrium between the coupler and borax giving an unreactive complex which results in lower apparent rate constants than those obtained from the reactions in other types of buffer. We found two other couplers which produced

complexes with borax: these have hydroxyl groups in either the 2,3- or 1,8- positions which indicates that the borate ion forms a cyclic complex with the two oxygen atoms of these groups.

The differences in the coupling rate constants of 4-chlorobenzenediazonium cation with a series of naphthalene-based couplers have been explained by the (often simultaneous) occurence of steric, mesomeric and inductive effects. Hammett plots were obtained from the reaction of a series of substituted arenediazonium cations with (XXX) indicating that use of the σ^+-constants is appropriate, which suggests that there is electron transfer from electron donating substituents to the diazonium group. Reaction constants ρ, were calculated for the reaction of both the singly- and doubly-ionised coupler to be 3.31 and 2.22 respectively.

(iii) The overall equilibrium between arenediazonium cations with their corresponding aryldiazotates is multi-stage, each consisting of at least six reactions as well as other reactions which may include the formation of a nitrosamine tautomer as the intermediate of the isomerisation of aryldiazohydroxides. We have found that investigation of this system is further complicated in two ways; (i) the aryldiazotates decompose by both photolysis and thermolysis to unknown products (possibly by a radical mechanism); (ii) we have also shown that the rate constants measured by following the formation of azo dye from the intermediate arenediazonium cation with a coupler are sometimes larger than those measured directly by the decrease in the concentration of aryldiazotate. Rate constants from this work were combined with those from the literature in order to determine the effect of ring substituents on certain rate and equilibrium constants. We ascertained that Hammett σ-constants give the best correlation with the rate constants k_1 of the

reaction of arenediazonium cations with OH^-, whereas σ^--constants are more appropriate for the isomerisation of syn-aryldiazotates to their anti- configuration, which suggests that there is some electron transfer from the diazotate group to electron-withdrawing substituents. We observed that the rate constants from the reactions of 2,6-dichloro-4-nitro compounds are lower than expected from the Hammett plots of the σ-constants versus log k_1, log k_{-1} and log k_3 possibly due to the steric effect of the 2- and 6-substituents, although we found that compounds with only one 2-substituent adhere to the linear free energy relationships.

In order to predict the most probable reaction pathways, a knowledge of as many rate and equilibrium constants as possible is essential and a list of these pertaining to the equilibrium between three substituted arenediazonium salts and their corresponding aryldiazotates are given in Table 30.

Table 30 shown overleaf

Table 30

Compiled rate and equilibrium constants for the equilibrium between three substituted arenediazonium cations and their corresponding aryldiazotates

Rate or equilibrium constants (abbreviations from Section 1.4)	Substituents		
	4-nitro	2-chloro-4-nitro	2-nitro-4-chloro
k_1 ($dm^3 mol^{-1} s^{-1}$)	3.7×10^5	1.67×10^6	6.31×10^5
k_{-1} (s^{-1})	ca. 2.0×10^2 (ref 119)	10	16
pK_1		8.78	9.40
pK_2		5.51	5.78
k_3 (s^{-1})	7.9×10^{-2}	3.2×10^{-2}	4.3×10^{-3} (ref 127)
k_{-3} (s^{-1})	5.03×10^{-4}	9.2×10^{-5} (ref 127)	3.7×10^{-4} (ref 127)
K_3	157	350	11.6
k_4 ($dm^3 mol^{-1} s^{-1}$)	9.3×10^2		
k_{-4} (s^{-1})	2.3×10^{-3} (ref 125)		
K_4 ($dm^3 mol^{-1}$)	3.9×10^{-9}		
K_5 ($mol\ dm^{-3}$)	6.75×10^{-7}		1.6×10^{-6} (ref 12
k_{-6} (s^{-1})	0.005	0.040	0.027 (ref 127)

4.2 Suggested further development in this field

Some problems arose in the course of this work which need clarification. The reactions between (XXX) and those arenediazonium cations with strongly electron-withdrawing substituents at pH 9.9 had coupling rate constants which were lower than expected from the Hammett plots. Such discrepancy may be due either to reactions being too fast for the stopped-flow apparatus to give accurate results or to a change in the rate-determining step of the reaction. This may be resolved by remeasurement of these rate constants with a more efficient stopped-flow apparatus (with a much shorter mixing time) and also the detection of general base catalysis by bases such as pyridine and determination of the hydrogen isotope effect, if any, with different substituted arenediazonium cations to ascertain whether there is a change from (35) to (34) (p20) as the rate-determining step with increasing size of the σ-constants.

We were unable to determine the rate constant k_{-1} of the N-O bond splitting of syn-4-nitro and 2-nitrobenzenediazohydroxides to their corresponding arenediazonium cations because these reactions were faster than the mixing time of the quenched stopped-flow apparatus. This could be overcome by the incorporation of a stop-syringe which should reduce this time very significantly and permit these values of k_{-1} to be measured. We were also unable to ascertain the nature of the products from the photolysis and thermolysis of anti-4-nitrobenzenediazotate or the radical intermediate detected during the former reaction, mainly because of limitation of time.

It would be of particular interest to study more fully the extremely efficient photolysis of the 4-nitrobenzenediazotate:

this might involve a mechanism:-

$$O_2NC_6H_4N_2O^- \xrightarrow{h\nu} O_2NC_6H_4^{\bullet} + N_2 + O^{\bar{\bullet}} \qquad (113)$$

although the nitrophenyl radical was not detected; moreover combination of this with $O^{\bar{\bullet}}$ to yield nitrophenol seems unlikely as the products were not phenolic. CIDNP studies could be very informative in elucidating the mechanism.

The study of the equilibrium between borax and(XXX) on p.116 was performed at only one pH value(5.6). It would be useful to examine this equilibrium at a selection of other pH values, notably at pHca. 8 at which borax has the largest influence on the coupling rate constants.

Finally, the gradient of Fig.33 was found to be less than the theoretical value of -2. To explain this anomaly further work will be required to find an alternative reaction pathway.

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Appendix

Observed and calculated structure factors and anisotropic temperature factors.

The observed and calculated structure factors are given below. Because of their length, final anisotropic temperature factor tables have been omitted and have been deposited with the British Library from where they are available.

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SODIUM SYN-DIAZOTATE-4-SULPHONATE

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FC	10FC	H	K	L	10FO	10FC
2	0	0	323	291	2	7	0	50	35	3	3	1	229	237	0	11	1	578	585	2	6	2	345	328
4	0	0	393	361	3	7	0	324	348	4	3	1	151	162	1	11	1	146	149	3	6	2	166	168
1	1	0	607	623	4	7	0	142	138	5	3	1	141	116	2	11	1	335	335	4	6	2	97	93
2	1	0	86	106	0	8	0	734	741	1	4	1	598	601	1	12	1	135	143	5	6	2	66	53
3	1	0	98	130	1	8	0	230	253	2	4	1	141	118	0	0	2	1024	1089	1	7	2	332	324
4	1	0	158	127	2	8	0	235	203	3	4	1	620	627	2	0	2	901	976	2	7	2	93	54
5	1	0	99	85	3	8	0	66	35	4	4	1	125	122	4	0	2	376	407	3	7	2	278	261
0	2	0	486	615	4	8	0	15	15	5	4	1	414	402	1	1	2	680	750	4	7	2	37	68
1	2	0	603	599	1	9	0	447	462	0	5	1	130	128	2	1	2	278	278	0	8	2	315	319
2	2	0	36	45	2	9	0	269	247	1	5	1	419	374	3	1	2	418	453	1	8	2	149	151
3	2	0	287	289	3	9	0	258	266	2	5	1	545	520	4	1	2	128	161	2	8	2	253	225
4	2	0	374	385	4	9	0	48	2	3	5	1	53	59	5	1	2	199	196	3	8	2	49	65
5	2	0	14	52	0	10	0	502	537	4	5	1	439	491	0	2	2	390	417	4	8	2	152	155
1	3	0	1017	976	1	10	0	92	95	5	5	1	50	59	1	2	2	278	279	1	9	2	497	482
2	3	0	54	24	2	10	0	120	114	1	6	1	437	433	2	2	2	378	419	2	9	2	229	219
3	3	0	704	687	3	10	0	228	232	2	6	1	231	255	3	2	2	40	68	3	9	2	91	62
4	3	0	92	96	1	11	0	165	147	3	6	1	155	150	4	2	2	169	147	4	9	2	112	104
5	3	0	348	337	2	11	0	60	34	4	6	1	14	31	5	2	2	85	77	0	10	2	294	275
0	4	0	604	611	0	12	0	378	372	5	6	1	35	96	1	3	2	567	541	1	10	2	30	23
1	4	0	630	611	1	12	0	43	35	0	7	1	773	774	2	3	2	325	315	2	10	2	100	97
2	4	0	144	104	2	0	1	1063	1022	1	7	1	156	129	3	3	2	714	769	3	10	2	95	32
3	4	0	37	18	4	0	1	326	350	2	7	1	481	484	4	3	2	32	35	1	11	2	184	181
4	4	0	218	229	0	1	1	301	375	3	7	1	121	134	5	3	2	296	295	2	11	2	49	52
5	4	0	88	101	1	1	1	702	749	4	7	1	405	405	0	4	2	223	211	0	12	2	121	127
1	5	0	11	8	2	1	1	279	265	1	8	1	134	121	1	4	2	610	577	1	12	2	83	73
2	5	0	389	390	3	1	1	253	271	2	8	1	230	234	2	4	2	641	644	2	0	3	703	659
3	5	0	224	175	4	1	1	141	152	3	8	1	319	326	3	4	2	185	183	4	0	3	296	285
4	5	0	159	175	5	1	1	181	197	4	8	1	99	110	4	4	2	191	171	0	1	3	206	206
5	5	0	30	12	1	2	1	759	796	0	9	1	292	271	5	4	2	80	69	1	1	3	377	374
0	6	0	204	156	2	2	1	168	178	1	9	1	155	151	1	5	2	375	349	2	1	3	282	300
1	6	0	314	282	3	2	1	365	350	2	9	1	155	157	2	5	2	403	382	3	1	3	345	331
2	6	0	47	50	4	2	1	59	26	3	9	1	90	109	3	5	2	206	239	4	1	3	157	161
3	6	0	15	8	5	2	1	112	104	4	9	1	54	62	4	5	2	72	53	5	1	3	221	235
4	6	0	205	208	0	3	1	1290	1261	1	10	1	124	128	5	5	2	107	99	1	2	3	447	491
5	6	0	41	21	1	3	1	507	452	2	10	1	146	162	0	6	2	326	345	2	2	3	206	180
1	7	0	548	524	2	3	1	135	141	3	10	1	133	178	1	6	2	560	543	3	2	3	383	416

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SODIUM SYN-DIAZOTATE-4-SULPHONATE

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	0	323	291	2	7	0	50	35	3	3	1	229	237	0	11	1	578	585	2	6	2	345	328
4	0	0	393	361	3	7	0	324	348	4	3	1	151	162	1	11	1	146	149	3	6	2	166	168
1	1	0	607	623	4	7	0	142	138	5	3	1	141	116	2	11	1	335	335	4	6	2	97	93
2	1	0	86	106	0	8	0	734	741	1	4	1	598	601	1	12	1	135	143	5	6	2	66	53
3	1	0	98	130	1	8	0	230	253	2	4	1	141	118	0	0	2	1024	1089	1	7	2	332	324
4	1	0	158	127	2	8	0	235	203	3	4	1	620	627	2	0	2	901	976	2	7	2	93	54
5	1	0	99	85	3	8	0	66	35	4	4	1	125	122	4	0	2	376	407	3	7	2	278	261
0	2	0	486	615	4	8	0	15	15	5	4	1	414	402	1	1	2	680	750	4	7	2	37	68
1	2	0	603	599	1	9	0	447	462	0	5	1	100	128	2	1	2	278	278	0	8	2	395	319
2	2	0	36	45	2	9	0	269	247	1	5	1	419	374	3	1	2	418	453	1	8	2	149	151
3	2	0	287	289	3	9	0	258	266	2	5	1	545	520	4	1	2	128	161	2	8	2	253	225
4	2	0	374	385	4	9	0	48	2	3	5	1	53	59	5	1	2	199	196	3	8	2	49	65
5	2	0	14	52	0	10	0	502	537	4	5	1	439	491	0	2	2	390	417	4	8	2	152	155
1	3	0	1017	976	1	10	0	92	95	5	5	1	50	59	1	2	2	278	279	1	9	2	407	482
2	3	0	54	24	2	10	0	120	114	1	6	1	437	433	2	2	2	378	419	2	9	2	229	219
3	3	0	704	687	3	10	0	228	232	2	6	1	231	255	3	2	2	40	68	3	9	2	91	62
4	3	0	92	96	1	11	0	165	147	3	6	1	155	150	4	2	2	169	147	4	9	2	112	104
5	3	0	348	337	2	11	0	60	34	4	6	1	14	31	5	2	2	85	77	0	10	2	294	275
0	4	0	604	611	0	12	0	378	372	5	6	1	35	96	1	3	2	567	541	1	10	2	30	23
1	4	0	630	611	1	12	0	43	35	0	7	1	773	774	2	3	2	325	315	2	10	2	100	97
2	4	0	144	104	2	0	1	1063	1022	1	7	1	156	129	3	3	2	714	769	3	10	2	95	32
3	4	0	37	18	4	0	1	326	350	2	7	1	481	484	4	3	2	32	35	1	11	2	184	181
4	4	0	218	229	0	1	1	301	375	3	7	1	121	134	5	3	2	296	295	2	11	2	49	52
5	4	0	88	101	1	1	1	702	749	4	7	1	405	405	0	4	2	223	211	0	12	2	121	127
1	5	0	11	8	2	1	1	279	265	1	8	1	134	121	1	4	2	610	577	1	12	2	83	73
2	5	0	389	390	3	1	1	253	271	2	8	1	230	234	2	4	2	641	644	2	0	3	703	659
3	5	0	224	175	4	1	1	141	152	3	8	1	319	326	3	4	2	185	183	4	0	3	286	285
4	5	0	159	175	5	1	1	181	197	4	8	1	99	110	4	4	2	191	171	0	1	3	206	206
5	5	0	30	12	1	2	1	759	796	0	9	1	292	271	5	4	2	80	69	1	1	3	377	374
0	6	0	204	156	2	2	1	168	178	1	9	1	155	151	1	5	2	375	349	2	1	3	282	300
1	6	0	314	282	3	2	1	365	350	2	9	1	155	157	2	5	2	403	382	3	1	3	345	331
2	6	0	47	50	4	2	1	59	26	3	9	1	90	109	3	5	2	206	239	4	1	3	157	161
3	6	0	15	8	5	2	1	112	104	4	9	1	54	62	4	5	2	72	53	5	1	3	221	235
4	6	0	205	208	0	3	1	1290	1261	1	10	1	124	128	5	5	2	107	99	1	2	3	447	491
5	6	0	41	21	1	3	1	507	452	2	10	1	146	162	0	6	2	326	345	2	2	3	206	180
1	7	0	548	524	2	3	1	135	142	3	10	1	133	178	1	6	2	560	543	3	2	3	383	416

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	2	3	200	227	3	9	3	201	174	3	5	4	235	312	4	1	5	258	261	3	8	5	302	282
5	2	3	290	263	4	9	3	47	72	4	5	4	107	97	5	1	5	71	50	4	8	5	95	61
0	3	3	143	118	1	10	3	210	214	5	5	4	56	63	1	2	5	828	792	0	9	5	189	206
1	3	3	805	760	2	10	3	112	118	0	6	4	547	516	2	2	5	226	244	1	9	5	154	157
2	3	3	463	457	3	10	3	174	183	1	6	4	279	262	3	2	5	369	363	2	9	5	161	160
3	3	3	122	119	0	11	3	272	282	2	6	4	312	314	4	2	5	188	213	3	9	5	152	144
4	3	3	228	232	1	11	3	162	169	3	6	4	158	163	5	2	5	433	424	1	10	5	267	278
5	3	3	107	134	2	11	3	294	280	4	6	4	231	277	0	3	5	318	300	2	10	5	130	129
1	4	3	433	428	1	12	3	224	209	5	6	4	155	168	1	3	5	489	463	3	10	5	221	219
2	4	3	185	187	0	0	4	688	721	1	7	4	272	314	2	3	5	451	445	0	11	5	169	162
3	4	3	301	307	2	0	4	596	562	2	7	4	197	212	3	3	5	83	92	1	11	5	246	239
4	4	3	114	134	4	0	4	430	432	3	7	4	271	273	4	3	5	392	389	2	11	5	71	75
5	4	3	346	341	1	1	4	645	657	4	7	4	19	22	5	3	5	103	131	1	12	5	197	134
0	5	3	268	317	2	1	4	490	461	0	8	4	153	158	1	4	5	372	363	0	0	6	829	865
1	5	3	231	239	3	1	4	457	448	1	8	4	72	61	2	4	5	229	222	2	0	6	344	295
2	5	3	304	336	4	1	4	144	167	2	8	4	151	166	3	4	5	528	556	4	0	6	292	244
3	5	3	25	62	5	1	4	368	395	3	8	4	14	51	4	4	5	144	148	1	1	6	596	616
4	5	3	375	364	0	2	4	784	777	4	8	4	175	172	5	4	5	181	181	2	1	6	240	262
5	5	3	81	112	1	2	4	323	294	1	9	4	534	532	0	5	5	682	685	3	1	6	489	501
1	6	3	381	385	2	2	4	263	295	2	9	4	92	99	1	5	5	147	135	4	1	6	90	129
2	6	3	13	24	3	2	4	233	229	3	9	4	252	258	2	5	5	359	357	5	1	6	282	279
3	6	3	228	229	4	2	4	264	297	4	9	4	15	46	3	5	5	190	207	0	2	6	1232	1201
4	6	3	47	73	5	2	4	35	42	0	10	4	241	250	4	5	5	681	698	1	2	6	254	231
5	6	3	173	177	1	3	4	640	585	1	10	4	93	116	5	5	5	70	56	2	2	6	238	237
0	7	3	324	333	2	3	4	176	170	2	10	4	196	193	1	6	5	406	415	3	2	6	194	183
1	7	3	204	205	3	3	4	191	177	3	10	4	128	136	2	6	5	118	149	4	2	6	250	237
2	7	3	380	391	4	3	4	115	124	1	11	4	249	246	3	6	5	327	346	5	2	6	167	165
3	7	3	131	135	5	3	4	249	204	2	11	4	183	171	4	6	5	129	147	1	3	6	269	229
4	7	3	348	359	0	4	4	330	326	0	12	4	198	199	5	6	5	149	144	2	3	6	148	149
1	8	3	50	62	1	4	4	623	612	1	12	4	37	81	0	7	5	479	481	3	3	6	92	40
2	8	3	210	215	2	4	4	441	441	2	0	5	632	647	1	7	5	79	71	4	3	6	92	67
3	8	3	194	190	3	4	4	230	247	4	0	5	152	154	2	7	5	102	76	5	3	6	57	96
4	8	3	117	115	4	4	4	67	83	0	1	5	131	123	3	7	5	188	197	0	4	6	596	530
0	9	3	112	99	5	4	4	104	130	1	1	5	538	533	4	7	5	196	194	1	4	6	265	255
1	9	3	55	39	1	5	4	188	190	2	1	5	119	116	1	8	5	253	238	2	4	6	182	189
2	9	3	150	159	2	5	4	320	321	3	1	5	235	278	2	8	5	133	146	3	4	6	179	146

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	4	6	242	245	3	1	7	218	216	3	8	7	80	89	5	4	8	171	157	4	2	9	195	104
5	4	6	82	66	4	1	7	355	364	4	8	7	76	63	1	5	8	135	160	5	2	9	193	111
1	5	6	523	503	5	1	7	169	187	0	9	7	211	199	2	5	8	13	39	0	3	9	595	556
2	5	6	196	198	1	2	7	334	788	1	9	7	70	71	3	5	8	298	313	1	3	9	179	121
3	5	6	104	85	2	2	7	368	363	2	9	7	53	64	4	5	8	14	28	2	3	9	495	417
4	5	6	238	241	3	2	7	223	223	3	9	7	50	21	0	6	8	316	325	3	3	9	123	146
5	5	6	165	168	4	2	7	188	196	1	10	7	212	216	1	6	8	356	369	4	3	9	344	346
0	6	6	135	133	5	2	7	143	128	2	10	7	132	122	2	6	8	226	233	5	3	9	55	38
1	6	6	346	346	0	3	7	213	196	3	10	7	81	99	3	6	8	77	58	1	4	9	575	594
2	6	6	315	294	1	3	7	171	196	0	11	7	58	54	4	6	8	239	245	2	4	9	134	129
3	6	6	70	79	2	3	7	506	506	1	11	7	55	66	1	7	8	246	241	3	4	9	373	386
4	6	6	347	359	3	3	7	103	75	2	11	7	32	45	2	7	8	124	109	4	4	9	76	85
1	7	6	72	62	4	3	7	339	344	0	0	8	914	852	3	7	8	195	193	5	4	9	276	234
2	7	6	192	175	5	3	7	15	16	2	0	8	335	384	4	7	8	15	33	0	5	9	159	123
3	7	6	223	224	1	4	7	338	311	4	0	8	34	97	0	8	8	231	262	1	5	9	156	134
4	7	6	171	154	2	4	7	87	91	1	1	8	828	819	1	8	8	108	96	2	5	9	368	358
0	8	6	559	545	3	4	7	210	200	2	1	8	429	437	2	9	8	397	398	3	5	9	94	19
1	8	6	94	79	4	4	7	84	69	3	1	8	79	74	3	8	8	90	93	4	5	9	255	260
2	8	6	206	214	5	4	7	149	133	4	1	8	53	66	1	9	8	369	383	1	6	9	299	210
3	8	6	203	211	0	5	7	443	430	5	1	8	259	255	2	9	8	179	183	2	6	9	169	151
4	8	6	198	194	1	5	7	238	212	0	2	8	801	752	3	9	8	155	182	3	6	9	691	607
1	9	6	457	449	2	5	7	455	468	1	2	8	227	226	0	10	8	241	249	4	6	9	29	36
2	9	6	80	94	3	5	7	104	107	2	2	8	345	337	1	10	8	19	24	0	7	9	292	179
3	9	6	255	239	4	5	7	403	394	3	2	8	35	76	2	10	8	328	309	1	7	9	136	126
0	10	6	597	578	5	5	7	38	31	4	2	8	197	215	1	11	8	272	286	2	7	9	256	267
1	10	6	124	111	1	6	7	305	309	5	2	8	15	26	2	0	9	358	374	3	7	9	87	92
2	10	6	258	263	2	6	7	98	78	1	3	8	255	278	4	0	9	280	296	4	7	9	147	176
3	10	6	90	97	3	6	7	280	278	2	3	8	153	154	0	1	9	244	278	1	8	9	93	67
1	11	6	115	127	4	6	7	54	50	3	3	8	37	51	1	1	9	396	355	2	8	9	178	176
2	11	6	78	75	0	7	7	295	286	4	3	8	100	96	2	1	9	567	610	3	8	9	126	110
0	12	6	262	246	1	7	7	249	225	5	3	8	79	66	3	1	9	159	160	0	9	9	67	55
2	0	7	344	359	2	7	7	106	101	0	4	8	322	313	4	1	9	414	420	1	9	9	104	106
4	0	7	123	118	3	7	7	68	73	1	4	8	349	343	5	1	9	147	140	2	9	9	150	151
0	1	7	764	712	4	7	7	25	59	2	4	8	188	192	1	2	9	586	538	3	9	9	54	60
1	1	7	455	414	1	8	7	333	327	3	4	8	51	55	2	2	9	347	374	1	10	9	294	203
2	1	7	511	516	2	8	7	166	152	4	4	8	95	104	3	2	9	123	114	2	10	9	171	163

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
0	11	9	112	105	2	7	10	106	111	2	5	11	310	290	2	4	12	90	55	3	3	13	50	64
1	11	9	104	124	3	7	10	133	126	3	5	11	34	64	3	4	12	89	93	4	3	13	203	294
0	0	10	826	809	4	7	10	15	47	4	5	11	105	114	4	4	12	139	125	1	4	13	279	270
2	0	10	160	150	0	8	10	521	506	1	6	11	255	255	1	5	12	203	212	2	4	13	171	138
4	0	10	244	233	1	8	10	69	82	2	6	11	128	121	2	5	12	117	124	3	4	13	294	309
1	1	10	505	532	2	8	10	529	522	3	6	11	398	406	3	5	12	317	334	4	4	13	39	38
2	1	10	263	257	3	8	10	88	62	4	6	11	50	69	4	5	12	120	121	0	5	13	247	230
3	1	10	353	350	1	9	10	119	115	0	7	11	191	155	0	6	12	144	135	1	5	13	203	194
4	1	10	131	131	2	9	10	50	56	1	7	11	235	238	1	6	12	162	166	2	5	13	366	373
5	1	10	191	175	3	9	10	88	78	2	7	11	153	165	2	6	12	180	191	3	5	13	171	130
0	2	10	170	145	0	10	10	287	302	3	7	11	31	64	3	6	12	108	95	4	5	13	152	110
1	2	10	25	44	1	10	10	104	117	1	8	11	92	99	1	7	12	254	242	1	6	13	369	367
2	2	10	284	303	2	10	10	310	327	2	8	11	94	143	2	7	12	120	113	2	6	13	34	38
3	2	10	49	64	2	0	11	269	246	3	8	11	93	79	3	7	12	107	113	3	6	13	355	343
4	2	10	61	91	4	0	11	134	176	0	9	11	21	63	0	8	12	573	576	0	7	13	193	217
5	2	10	157	154	0	1	11	547	518	1	9	11	76	60	1	8	12	94	95	1	7	13	190	106
1	3	10	307	298	1	1	11	231	223	2	9	11	51	55	2	8	12	267	266	2	7	13	294	230
2	3	10	253	254	2	1	11	504	494	1	10	11	217	214	3	8	12	85	80	3	7	13	62	70
3	3	10	216	203	3	1	11	219	223	0	0	12	705	719	1	9	12	66	72	1	8	13	91	78
4	3	10	103	94	4	1	11	241	233	2	0	12	254	248	2	9	12	15	31	2	8	13	95	26
5	3	10	216	204	5	1	11	36	52	4	0	12	127	121	0	10	12	288	265	0	9	13	294	184
0	4	10	130	95	1	2	11	407	395	1	1	12	409	388	1	10	12	86	87	1	9	13	164	151
1	4	10	291	292	2	2	11	81	79	2	1	12	35	50	2	0	13	44	43	0	0	14	392	279
2	4	10	247	253	3	2	11	92	96	3	1	12	276	277	4	0	13	243	256	2	0	14	345	334
3	4	10	231	223	4	2	11	141	153	4	1	12	51	44	0	1	13	320	323	4	0	14	195	206
4	4	10	86	96	0	3	11	378	406	0	2	12	202	187	1	1	13	145	160	1	1	14	535	557
1	5	10	332	322	1	3	11	462	465	1	2	12	222	227	2	1	13	290	300	2	1	14	156	165
2	5	10	418	415	2	3	11	407	414	2	2	12	199	182	3	1	13	105	118	3	1	14	267	257
3	5	10	337	321	3	3	11	115	100	3	2	12	303	308	4	1	13	231	248	4	1	14	77	55
4	5	10	38	74	4	3	11	264	257	4	2	12	14	42	1	2	13	109	113	0	2	14	443	445
0	6	10	97	63	1	4	11	360	364	1	3	12	57	41	2	2	13	128	116	1	2	14	173	171
1	6	10	333	320	2	4	11	82	110	2	3	12	157	150	3	2	13	319	309	2	2	14	368	358
2	6	10	152	155	3	4	11	447	439	3	3	12	334	340	4	2	13	67	73	3	2	14	94	36
3	6	10	229	228	4	4	11	40	64	4	3	12	228	236	0	3	13	388	379	4	2	14	85	72
4	6	10	94	59	0	5	11	217	235	0	4	12	157	198	1	3	13	237	242	1	3	14	199	177
1	7	10	390	380	1	5	11	126	132	1	4	12	110	118	2	3	13	482	478	2	3	14	171	154

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
3	3	14	212	207	3	1	15	34	15	0	0	-6	296	306	0	1	17	149	167	1	2	18	235	208
4	3	14	34	38	4	1	15	30	74	2	0	-6	324	334	1	1	17	31	51	2	2	18	168	180
0	4	14	409	377	1	2	15	362	358	1	1	-6	224	220	2	1	17	152	163	1	3	18	192	191
1	4	14	177	171	2	2	15	17	40	2	1	-6	137	194	3	1	17	65	34	2	3	18	34	30
2	4	14	228	231	3	2	15	329	313	3	1	-6	253	254	1	2	17	123	146	0	4	18	171	156
3	4	14	54	59	4	2	15	67	66	0	2	-6	232	278	2	2	17	86	84	1	4	18	193	98
1	5	14	245	225	0	3	15	157	145	1	2	-6	198	194	3	2	17	306	317	2	4	18	171	131
2	5	14	104	119	1	3	15	71	94	2	2	-6	199	206	0	3	17	233	207	1	5	18	82	68
3	5	14	203	204	2	3	15	453	463	3	2	-6	78	101	1	3	17	230	214	0	6	18	203	186
0	6	14	448	437	3	3	15	66	53	1	3	-6	157	141	2	3	17	80	96	2	0	19	15	16
1	6	14	101	119	1	4	15	83	80	2	3	-6	14	20	3	3	17	151	138	0	1	19	146	137
2	6	14	210	210	2	4	15	180	205	3	3	-6	227	241	1	4	17	139	130	1	1	19	171	121
3	6	14	106	113	3	4	15	311	301	0	4	-6	249	234	2	4	17	63	17	2	1	19	83	101
1	7	14	183	147	0	5	15	682	666	1	4	-6	135	170	0	5	17	34	48	1	2	19	238	216
2	7	14	15	5	1	5	15	71	54	2	4	-6	237	266	1	5	17	151	144	2	2	19	72	83
0	8	14	420	415	2	5	15	292	297	3	4	-6	135	132	2	5	17	262	278	0	3	19	15	8
1	8	14	153	108	3	5	15	77	63	1	5	-6	105	129	1	6	17	106	107	1	3	19	157	144
2	8	14	352	327	1	6	15	274	283	2	5	-6	214	210	0	7	17	198	204	1	4	19	251	271
1	9	14	273	289	2	6	15	15	53	0	6	-6	250	266	0	0	18	429	445	0	5	19	76	83
2	0	15	363	353	3	6	15	299	307	1	6	-6	111	102	2	0	18	214	204	0	0	20	482	445
4	0	15	92	95	0	7	15	131	112	2	6	-6	198	185	1	1	18	251	256	1	1	20	156	165
0	1	15	383	359	1	7	15	35	41	1	7	-6	58	78	2	1	18	124	111	0	2	20	131	130
1	1	15	282	287	2	7	15	78	78	0	8	-6	243	193	0	2	18	183	194	1	2	20	97	71
2	1	15	192	186	1	8	15	111	106	2	0	-7	128	142										